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- (A) COLORED UNSATURATED POLYESTER MATERIAL CONTAINING COPOLYMERIZED METHINE DYES, AND PRODUCTS THEREFROM.
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Chemical Abstract, volume 71, no. 12, 22 September 1969, (Columbus, Ohio, US), V.V. Korshak et al.: "Colored polyesters based on bis (hydroxyalkoxy) azo-benzenes", see page 24, abstract no. 50783u, & Izv. Akad. Nauk SSSR, Ser. Khim. 1969, (5), 1078-85

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#### Description

This invention relates to colored, unsaturated polyesters which contain certain methine dye moieties chemically linked through copolymerization into the polyester backbone whereby the dye moieties become essentially nonextractable from the polyester. These colored polyesters are thus highly suitable for incorporation into curable polyester materials used in the production of bathroom fixtures (sinks, showers, tubs), boats, automotive parts, and the like wherein resistance to dye extractability is of great consequence. The addition of the methine dye monomers during the polyester preparation also gives greater colorant uniformity than possible, for example, where such colorants are simply blended with the polyester material prior to casting or molding thereof.

It is known, of course, that some methine dyes may be used to color polyester fibers using conventional dyeing procedures. It is also known that certain dyes can be melt blended (not copolymerized) with preformed polyesters or dispersed with reactive solvent (curing monomer) into unsaturated polyester material prior to molding and curing, to produce colored product. In other limited cases, certain dyes such as selected anthraquinones are reactable into the polyester chain by copolymerization.

Advantages of the present methine moieties over others which might be copolymerized into the polyester include (1) greater thermal stability, for example, than azo dyes which generally are not stable to polymer preparation temperatures, (2) methine dyes can be selected or tailored to absorb light at the proper wavelengths to protect particular contents of a package, (3) certain anthraquinone dyes, for example, which absorb light below 420 nm are generally not stable to UV, (4) the present methine dyes have high extinction coefficients, i.e., less dye is needed to give equivalent color, and (5) generally speaking, methine dyes are much less costly than anthraquinone dyes.

In accordance with the present invention, the methine moieties have at least one methine unit defined herein as "the group >C=C< conjoined with a conjugated aromatic system." This unit imparts to the moiety and to the polymer the property of ultraviolet or visible light absorption generally within the range of about 320 nm to about 650 nm. The moieties preferably have molecular weights of from about 200 to about 600 although lower and higher molecular weights are also operable. The moieties are derived from reactants (monomers) having one or more groups which condense during esterification or polycondensation to enter the moiety into the polymer chain. These groups include hydroxyl, carboxyl, carboxylic ester, acid halide, amino and the like. As aforesaid, these methine moieties are thermally stable at polymer processing conditions, for example, including polycondensation temperatures of up to about 300°C. Of course, where only one condensable group is present, the methine monomer would act as a chain terminator in known manner. These moieties are useful in total concentrations ranging from about 1.0 to about 5,000, preferably 2.0 to about 1,500 parts by weight of moiety per million parts by weight of final polymer (ppm).

The present invention is defined in its broad embodiment as unsaturated polyester material having copolymerized therein a total of from 1.0 to about 5,000 ppm, of at least one methine moiety having one or more methine units, said moiety absorbing in the range of from 320 nm to about 650 nm, and being non-extractable from said polyester material and stable under processing conditions therefor.

The extractabilities of the present methine moieties can be determined as follows:

#### **Extraction Procedure**

All extractions are done in glass containers with distilled solvents (water, heptane, etc.) under the time and temperature conditions described below. The sample form is 0.5 inch  $\times$  2.5 inch (12.7  $\times$  63.5 mm) molded segments of about 10 to 20 ml thickness, the thickness, however, not being critical. All samples are washed with cold solvent to remove surface contaminants and are then contacted with 2 ml of solvent/inch² (1 ml of solvent/3.2 cm²) of surface area. After the specified period of ageing in the solvent, the solvent is transferred to glass flasks, concentrated, spiked and analyzed. Solvent blanks (controls) are run under the same conditions without polymer.

#### **Extraction Conditions**

- 1. Water. The samples are added to the solvent at room temperature and heated at 250°F (121°C) (15 psi, 1.03 bar) for two hours. For half the samples, the solvent is transferred to glass flasks, concentrated, and analyzed; the remaining samples are placed in a 120°F (49°C) oven for 30 days and the solvent then transferred to glass flasks, concentrated, and analyzed.
- 50% Ethanol/water (v/v). The samples are added to solvent at room temperature, placed in an oven at 120°F (49°C), concentrated, and analyzed after 24 hours and 30 days.
  - 3. Heptane. The samples are added to solvent at 150°F (65°C) and heated at 150°F (65°C) for 2 hours. Part of the samples are transferred to glass flasks, concentrated, and analyzed. The remainder of the samples are placed in a 120°F (49°C) oven for 30 days and the solvent then transferred to glass flasks, concentrated, and analyzed.

**Analysis** 

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Instrument — Hewlett-Packard 8450A spectrophotometer

Cell Path Length — 1 cm Scanning Range — 400 nm to 650 nm

Calibration for Red Methine dye in Anisole - 520 nm absorbance maximum

Calibration for Red Methine dye in DMF - 530 nm absorbance maximum

The Hewlett-Packard 8450 A spectrophotometer is equipped with microprocessor and programming capability with RAM memory and floppy disk storage. The instrument is calibrated at 1000 ppb, 1500 ppb, and 2000 ppb dye in anisole and 970 ppb, 1460 ppb, and 1940 ppb in the DMF. The calibration data are 10 stored on a floppy disk for recall when needed.

The extractability of the present methine moieties from the present cured polyester material is essentially nonexistent.

Useful methine reactants or monomers for the present invention have the general formulas:

wherein A is selected from the following radicals designated by their exemplary table numbers:

(Shown in Table 11)

(R) 
$$\frac{1}{n}$$
  $\frac{1}{n}$   $\frac{1}{n}$ 

$$(R)_{n} \stackrel{R_{1}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}}{\stackrel{R_{1}}}}{\stackrel{R_{1}}}{\stackrel{R_{1}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$$

(10)

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R and R' are selected from hydrogen, fluorine, chlorine, bromine, alkyl, alkoxy, phenyl, phenoxy, alkythio, and arylthio; n is 0, 1, 2;

(15)

 $R_1$  and  $R_2$  are selected from hydrogen; cycloalkyl; cycloalkyl substituted with one or two of alkyl, —OH, n<sub>1</sub> and n<sub>2</sub> are selected from hydrogen; cycloalky; cycloalky; substituted with old of two dalky, alkoxy, halogen, or hydroxy substituted alkyl; phenyl; phenyl; substituted with alkyl, alkoxy, halogen, alkanoylamino, carboxy, cyano, or alkoxycarbonyl; straight or branched lower alkenyl; straight or branched alkyl of 1—8 carbons and such alkyl substituted with the following: hydroxy; halogen; cyano; succinimido; hydroxysuccinimido; acyloxysuccinimido; glutarimido; phenylcarbamoylox; phthalimido; 4-carboxyphthalimido; phthalimidino; 2-pyrrolidono; cyclohexyl; phenyl; phenyl substituted with alkyl, alkoxy, halogen, hydroxy alkanoylamino; carboxy, cyano, or alkoxycarbonyl; alkylsulfamoyl; vinylsulfonyl; acrylamido; sulfamyl; benzoylsulfonicimido; alkylsulfonamido; phenylsulfonamido; alkoxycarboxylamino; carboxylamino; ca carbonylamino; alkylcarbamoyloxy; alkoxycarbonyl; alkoxycarbonyloxy; alkenylcarbonylamino; groups of the formula

wherein Y is -NH-,

-, or —CH<sub>2</sub>O—; —S—R<sub>14</sub>; SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SR<sub>14</sub>; wherein R<sub>14</sub> is alkyl, phenyl, phenyl substituted with halogen, alkyl, alkoxy, alkanoylamino, cyano, or alkoxycarbonyl; pyridyl; pyrimidinyl; benzoxazolyl; benzimidazoylyl; benzothiazolyl; radicals of the formulae

 $-OXR_{16}$ ;  $-NHXR_{16}$ ;  $-X-R_{16}$ ;  $-CONR_{15}R_{15}$ ; and  $-S_2NR_{15}R_{15}$ ; wherein  $R_{15}$  is selected from H, aryl, alkyl, and alkyl substituted with halogen, -OH, phenoxy, aryl, -CN, cycloalkyl, alkylsulfonyl, alkylthio, alkanoyloxy, or alkoxy; X is -CO-, -COO-, or  $-SO_2$ ;  $R_{16}$  is selected from alkyl and alkyl substituted with halogen, hydroxy, phenoxy, aryl, cyano, cycloalkyl, alkylsulfonyl, alkylthio, alkanoyloxy, and alkoxy; and when X is -CO-,  $R_{16}$  also can be hydrogen, amino, alkenyl, alkylamino, dialkylamino, arylamino, aryl, or furyl; alkoxy, alkoxy substituted with hydroxy, cyano, alkanoyloxy, or alkoxy; phenoxy; phenoxy substituted with one or more of alkyl, carboxy, alkoxy, carbalkoxy, or halogen;  $R_1$  and  $R_2$  can be a single combined group such as pentamethylene, tetramethylene, ethyleneoxyethylene, ethylene sulfonylethylene, or

-N-ethylene ethylene-

which, with the nitrogen to which it is attached, forms a ring; R<sub>17</sub> is alkyl, aryl, or cycloalkyl;

R<sub>3</sub> is alkylene, arylene, aralkylene, alkyleneoxy, or alkyleneoxyalkylene;

Z is a direct single bond, OCO, O, S, SO<sub>2</sub>, R<sub>17</sub>SO<sub>2</sub>N=,

arylene, or alkylene; 35

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 $R_4$ ,  $R_5$ , and  $R_6$  are each selected from hydrogen and alkyl;

R7 is carboxy, carbalkoxy, or (R),;

R<sub>10</sub> is hydrogen, alkyl, and aryl;

 $R_8$  and  $R_9$  are selected from hydrogen and substituted or unsubstituted alkyl, aryl, or cycloalkyl;

 $R_{11}$  and  $R_{12}$  are hydrogen, alkyl, hydroxyl, or acyloxy;

B represents the atoms necessary to complete a five or six membered ring and is selected from

P and Q are selected from cyano, carbałkoxy, carbaryloxy, carbaralkyloxy, carbamyl, carboxy, N-alkyl-carbamyl, N-alkyl-N-arylcarbamyl, N,N-dialkylcarbamyl, N-arylcarbamyl, N-cyclohexylcarbamyl, aryl, 2-benzoxazolyl, 2-benzothiazolyl, 2-benzimidazolyl, 1,3,4-thiadiazol-2-yl, 1,3,4-oxadiazol-2-yl, SO<sub>2</sub> alkyl, SO<sub>2</sub> aryl, and acyl, or P and Q may be combined as

$$= C \qquad \qquad C$$

wherein R<sub>17</sub> is defined above and R<sub>18</sub> is CN, COOH, CO<sub>2</sub> alkyl, carbamyl, or N-alkylcarbamyl;

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wherein at least one of A, P, and Q for each dye molecule must be or bear a condensable group selected from carboxy, carbalkoxy, carbaryloxy, N-alkylcarbamyloxy, acyloxy, chlorocarbonyl, carbamyloxy, N-(alkyl)<sub>2</sub>carbamyloxy, amino, alkylamino, hydroxyl, N-phenylcarbamyloxy, cyclohexanoyloxy, and carbocyclohexyloxy; and

wherein in the above definitions, each alkyl, aryl, or cycloalkyl moiety or portion of a group or radical may be substituted where appropriate with hydroxyl, acyloxy, alkyl, cyano, alkoxycarbonyl, halogen, alkoxy, or aryl, aryloxy, or cycloalkyl. Also in the above definitions, at least one of A, P, and Q for each dye molecule must be or bear a group capable of reacting under polymerization conditions, to incorporate the methine dye into the polymer, including the following, carboxy, carbalkoxy, carbaryloxy, N-alkylcarbamyloxy, acyloxy, chlorocarbonyl, carbamyloxy, N-alkylcarbamyloxy, amino, alkylamino, hydroxyl, N-phenylcarbamyloxy, cyclohexanoyloxy, and carbocyclohexyloxy, wherein the alkyl and/or aryl groups may contain common substituents such as hydroxyl, cyano, acyloxy, carbalkoxy, phenyl, and halogen which do not interfere with the condensation reaction.

In all of the above definitions the alkyl or alkylene moleties or portions of the various groups contain from 1—8 carbons, straight or branched chain.

The unsaturated polyesters useful in this invention include the esterification and polycondensation products of one or more unsaturated dicarboxylic acids or their anhydrides and one or more dihydric or polyhydric alcohols. As the acid component, the  $\alpha,\beta$ -ethylenically unsaturated polycarboxylic acids include those having 2—12 carbon atoms, e.g., maleic, fumaric, substituted fumaric, citraconic, mesaconic, tetraconic, glutaconic, muconic, and the like, as well as mixtures thereof. Noncurable polycarboxylic acids, i.e., those which do not contain reactive  $\alpha,\beta$ -ethylenic unsaturation, may also be used if employed in combination with one or more of the aforementioned  $\alpha,\beta$ -ethylenically unsaturated polycarboxylic acids. Where such noncurable polycarboxylic acids are employed, the amount thereof should not constitute more than about 80% of the total equivalents of carboxyl groups in the esterification mixture. Preferably, such noncurable polycarboxylic acids will be employed in amounts varying between about 35% and 75% of the above indicated equivalence basis. Among the noncurable polycarboxylic acids that may be used are oxalic, malonic, succinic, glutaric, sebacic, adipic, phthalic, isopthalic, terephthalic, substituted phthalic, such as tetrachlorophthalic, suberic, azelaic, tricarballylic, citric, tartaric, cyclopropanedicarboxylic, cyclohexanedicarboxylic, and the like, as well as mixtures thereof.

As the alcohol component, the saturated aliphatic polyhydric alcohols include those preferably containing only two hydroxyl groups. Among such diols are ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, butanediol-1,2, butanediol-1,3, butanediol-1,4, pentanediol-1,4, pentanediol-1,5, hexanediol-1,6, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol and the like, as well as mixtures thereof. However, saturated aliphatic polyhydric alcohols containing more than two hydroxyl groups may also be employed and include glycerol, trimethylol ethane, trimethylol propane, pentaerythritol, sorbitol, and the like, as well as mixtures thereof. It is usually desirable that such polyols be employed in minor proportions relative to the diol or diols.

The components may be reacted in the manner customarily used in preparing ethylenically unsatruated polyester resins, i.e., at elevated temperatures and atmospheric pressure, although pressures slightly above or below atmospheric may be employed if desired. The reaction temperature is not critical but preferably is just below the boiling point of the most volatile component of the reaction mixture which is generally the alcohol component. However, temperatures in excess of the boiling point of the most volatile constituent may be employed if the reaction vessel has been equipped with a steam-heated reflux condenser which permits water of esterification to escape from the reaction vessel while condensing volatilized reaction components and returning them to the reaction system.

In preparing the curable compositions, the unsaturated polyesters are blended with a reactive curing agent, operably in a weight ratio of agent/polyester of 10/90 to 90/10, but preferably from 30/60 to 70/40. These agents contain one or more CH<sub>2</sub>=C< groups and desirably have boiling points at atmospheric pressure of 60°C or greater. Such agents include styrene, side-chain substituted styrenes such as the α-methyl styrene, α-ethyl styrene, and the like, ring substituted styrenes, such as alkyl styrenes, e.g., ortho-

meta and para-alkyl styrenes, including o-methyl styrene, p-ethyl styrene, meta-propyl styrene, 2,4-dimethyl styrene, 2,5-diethyl styrene, and the like, halostyrenes, e.g., o-bromostyrene, p-chlorostyrene, 2,4-dichlorostyrene, and the like. Also included are alkyl esters of acrylic and methacrylic acid, e.g., methyl, ethyl, or butyl acrylate, methyl methacrylate, and the like. Also useful are vinyl acetate, vinyl butyrate, vinyl laurate, acrylonitrile, methacrylonitrile, vinyl chloride, acrylamide, methacrylamide and their dderivatives, allyl compounds such as diallyl phthalate, allyl acetate, allyl methacrylate, diallyl carbonate, allyl lactate, allyl acrylate, diallyl methacrylate, diallyl oxalate, diallyl oxalate, diallyl oxalate, diallyl oxalate, diallyl methyl gluconate, diallyl adipate, diallyl sebacate, diallyl tartronate, diallyl tartrate, diallyl mesaconate, diallyl citraconate, the diallyl ester of muconic acid, diallyl itaconate, diallyl chlorophthalate, tricarballylate, triallyl rimesate, triallyl ester of endomethylenetetrahydrophthalic anhydride, triallyl methyallyl phosphate, tetraallyl siliane, tetraallyl silicate, hexallyldisiloxane, and the like. These curing agents may be used singly or in combination with one another.

In order to facilitate the curing, it is preferred that a polymerization catalyst be incorporated in the blend at the time of its curing. The type and amounts of these catalytic materials are well known in the art, and any material which normally induces polymerization of polyester resinous compositions can be utilized. The optimum reaction conditions are modified to some extent by the choice of the particular catalyst used in the process. A very active catalyst should be used in lower concentrations, and preferably at lower temperatures, than a less reactive material. The preferred catalysts comprise a wide variety of organic superoxides, i.e., organic peroxides ("acidic peroxides") and hydroperoxides ("alcoholic peroxides"). Mixtures of peroxides and hydroperoxides, including commercially available mixtures such as methyl ethyl ketone peroxide, cyclohexanone peroxide, and the like, are especially effective as catalysts. Among the useful organic peroxide catalysts are acetyl peroxide, benzoyl peroxide, substituted benzoyl peroxides, halogenated benzyl peroxides such as p-bromobenzoyl peroxide, and 2,4-dichlorobenzoyl peroxide, benzoyl acetyl peroxide, phthalyl peroxide, succinyl peroxide, fatty oil acid peroxides, such as coconut oil peroxide, lauryl peroxide, stearyl peroxide, oleyl peroxide, anisoyl peroxide, toluyl peroxide, and the like. Organic peracids, such as peracetic acid and perbenzoic acid, may also be employed. The useful organic hdyroperoxide catalysts include tertiary butyl hydroperoxide, cumene hydroperoxide, diisopropyl benzene hydroperoxide, 1-hydroxycyclohexyl hydroperoxide, the terpene oxides, such as ascaridole, 1-p-methane hydroperoxide, and the like. Various other types of polymerization catalysts may also be employed, for example, compounds such as aluminum chloride, stannic chloride, boron trifluoride, or the azo-type catalysts such as a,a'-azobisisobutyronitrile.

Since the unsaturated polyester may contain a high degree of polymerizable or reactive unsaturation, it is often desirable to bland a polymerization inhibitor therewith to retard internal polymerization of the polyester during any storage period encountered prior to curing. Once the curable composition is contacted with a sufficient amount of a polymerization catalyst, however, the effect of the inhibitor will be overcome. Among the useful inhibitors are phenol, the monoalkyl phenols, such as ortho-, meta-, and paracresol as well as mixtures of such isomers, polyalkyl phenols having a plurality of the same or different substituents, e.g., ethyl, propyl, butyl, and higher alkyl radicals attached to their nuclei, catechol, tertiary butyl catechol, hydroquinone, tertiary butyl hydroquinone, resorcinol, eugenol, guaiacol, pyrogallol, benzaldehyde, tannic acid, ascorbic acid, isoascorbic acid, phenylene diamine, sym-di-β-naphthyl-phenylene diamine, aniline, and the like. The amount of polymerization inhibitor employed depends on the nature of the unsaturated polyester as well as the period of storage stability required. Generally, from about 0.001% to 0.3% by weight, based on the total weight of the curable polyester blend will be sufficient.

Inhibitors of this type may be added during preparation of the unsaturated polyester or optionally added later to the curable blend. In addition, other known additives may be employed such as promoters used in conjunction with the catalyst, mold lubricants, fillers and reinforcing materials, other colorants, flow promoters, ultraviolet absorbing agents, and the like.

The conditions necessary for curing the above blends do not depart from the practice ordinarily observed in curing these types of compositions in general. They may be cured in contact with air or in enclosed molds at temperatures ranging from about 10°C to about 160°C, or even higher as long as they are kept below the point at which the particular curable blend employed begins to decompose. Where it is convenient, it is especially desirable to cure the catalyzed blends by heating to between 90°C and about 150°C for a period of about 3 to 90 minutes.

In general, the methine reactants (monomers) are prepared, for example, by reacting the hydrogenated parent of an aromatic moiety A above, which is electron rich, with a Vilsmeier complex to produce an aldehyde [Bull. Societe Chim. de France, No. 10:1898—99 (October 1962); Angewandte Chemie 72, No. 22, 836—845, November 21, 1960]. For reasons of cost and convenience, phosphorus oxychloride (POCl<sub>3</sub>) and N,N-dimethylformamide (DMF) are the preferred reagents. Thus, aromatic amines such as anilines, m-toluidines, 2,5-dimethylanilines, 2,5-dimethoxyanilines, or the like are converted in high yields into the corresponding aldehydes via the Vilsmeier reaction, which aldehydes are subsequently reacted with an active methylene compound of the formula P—CH<sub>2</sub>—Q in the presence of a base, such as piperidine to produce the methine monomers, as shown in the following reaction sequence

Tetrahydroquinolines, benzomorpholines, indoles, thiazoles, and Fischer's base also undergo the Vilsmeier reactions to produce aldehydes. Preparation of the methine monomers and intermediate aldehydes via the above route is disclosed in considerable detail in many patents including: U.S. 2,649,471; U.S. 2,850,520; U.S. 3,247,211; U.S. 3,260,737; U.S. 3,326,960; U.S. 3,349,098; U.S. 3,386,491; U.S. 3,390,168; U.S. 3,453,270; U.S. 3,453,280; U.S. 3,468,619; U.S. 3,504,010; U.S. 3,555,016; U.S. 3,597,434; U.S. 3,652,636; U.S. 3,661,899; U.S. 3,728,374; U.S. 3,787,476; U.S. 3,829,410; U.S. 3,829,461; U.S. 3,846,069; U.S. 3,869,495; U.S. 3,869,498; U.S. 4,879,434; U.S. 3,920,719; and U.S. 4,077,962. It is also known that it is not necessary to isolate the intermediate aldehyde before preparing the methine monomers as the Vilsmeier reaction mixture can be reacted directly to produce the desired product (U.S. Patents 3,917,604 and 4,088,673). All of these patent teachings are incorporated herein by reference.

Since the Vilsmeier complexes also convert hydroxyl groups to halogen, other methods must be employed to prepare methine monomers bearing hydroxyl groups. For example, the monomers can be prepared according to the scheme

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comprising reacting N,N-di-β-hydroxyethylaniline with formaldehyde and m-nitrobenzenesulfonic acid in the presence of concentrated HCl and iron filings to produce the intermediate 4'-(di-β-hydroxyethylamino)-benzalaniline-m-sulfonic acid, which can be reacted with active methylenes to produce the monomers (U.S. 2,583,551).

Another method for producing methine monomers containing dicyanovinyl groups is described in U.S. 4,006,178 wherein aromatic amines are reacted with 1-halogeno-2,2-dicyanoethylene to produce corresponding methine compounds as follows:

$$(R)_{n} = R_{1} + Hal.-CH=CCN$$

$$(R)_{n} = R_{1} + Hal.-CH=CN$$

$$(R)_{n} = R_{1}$$

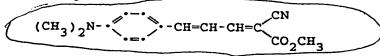
$$(R)_{n} = R_{1}$$

Intermediate aldehyde compounds containing groups such as acyloxy or alkoxycarbonyl can be hydrolyzed to prepare methine monomers containing hydroxyl or carboxy groups, respectively, which are capable of being reacted into the condensation polymer.

The following examples will illustrate the common reaction of an aromatic aldehyde with an active methylene to produce a typical methine monomer.

Example 1

4-(N,N-Dimethylamino)cinnamaldehyde (1,75 g, 0.01 m), methyl cyanoacetate (0.99 g, 0.01 m), methanol (20 mL), and piperidine (3 drops) are mixed and heated together at reflux for 30 minutes. After being allowed to cool, the reaction mixture is filtered. The orange dye (2.5 g) is washed with methanol and air-dried and has the following structure.



This yellow dye absorbs light at  $\lambda_{max}$  464 nm with a molar extinction coefficient of 38,000.

Example 2

Ethyl [[4-(dimethylamino)phenyl]methylene]propenedioate shown below is prepared by the reaction of 4-(dimethylamino)benzaldehyde with diethyl malonate in the presence of a base catalyst in toluene. This pale yellow dye absorbs UV light at  $\lambda_{max}$  373 nm with a molar extinction coefficient of 33,000.

The following tables further exemplify the useful methine reactants.

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		0 'd	CN, CN	CN, CONHC6Hs	CN, SO <sub>2</sub> CH <sub>3</sub> CN, COC <sub>6</sub> H <sub>5</sub>	CN, NO	CN, CO2CH,	CN, CONH2	CN, CO2C2Hs	CN, CO2C6H5	CN, CO2C6H11	CN, CONHC2H, OH
TABLE 1	1	R2	CH <sub>2</sub> CH <sub>2</sub> OH CH <sub>2</sub> CH <sub>2</sub> OH	CH2CH2OH	CH <sub>2</sub> CH <sub>2</sub> OH CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>2</sub> CH <sub>2</sub> OH	C2H5	C2Hs	C2Hs	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C2H <sub>5</sub>
	C=CH-YOUNG	F.	CH <sub>2</sub> CH <sub>2</sub> OH	CH2 CH2 OH	CH <sub>2</sub> CH <sub>2</sub> OH	СН2СН2ОН	СН 2СН (ОН)СН 3	CH2CH(OH)CH2OH	C2Hs	C2 = 5	ر <sub>2</sub> n s	C <sub>2</sub> H <sub>5</sub>
		-	× =	3-CH,	· =	<b>=</b>	3-CH <sub>3</sub>	2,5-d1-0CH3	2-0CH 5-Ch	2-SCH-	2-0C u	7_0rens
-		xample No.	J 44	o n	7	89	σ (	1 1	1 1	7 F	7 -	<b>.</b>

. Ссн., ссн	CN, CO <sub>2</sub> CH <sub>3</sub> CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CN
TABLE 1 (continued)  C2H, OCCH, CH2CH2OCCH,	CH <sub>2</sub> CH <sub>2</sub> OH CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH2
	m-ClC <sub>6</sub> H, CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
е (R)	3-CH,	3-CH3
Example No. 15 16 17 19 20 21 22 23 23	26	87

inued)	R2 P, Q	CH2 CO2CH3 CN, COC(CH3)3	о сн <sub>2</sub> сн <sub>2</sub> оссн <sub>3</sub> си, со <sub>2</sub> сн <sub>3</sub>	CH2CH2OCC6H3 CN, CO2CH2OCH3	C2H3 CN, CO2CH3	C2Hs CN, CO2CH,		C2H3 CN, CO2CH3	CH2CH2CO2CH3				CH2	CH2 COC1 CN, CN	TO CO TRIB
TABLE 1 (continued)	R]	CH2	CH2	CH2()OCH3 C	CH, CH, OCC, H,	CH2CH2OCNHC6H3 C		CH2CH2CN C	CH2CH2CO2CH3 CI	CH2CH2CO2H CI			CH2	CH2	,CH,CH
-	(R) <sub>n</sub>	3-CH3	3-CH <sub>3</sub>	3-CH <sub>3</sub> .	3-сн,	3-сн,	; = =	3-CH3	==	×	æ	æ	æ	<b>=</b>	=
Example	No.	29	30	31	32	33	34	C	36	37	38	39	40	41	42

	P , Q	CN, CO2CH	CN, CO2CH1	CN, CO2CH3	CN, CO <sub>2</sub> CH,	<i>,,</i>	CN, CO2CH3	SO <sub>2</sub> CH <sub>3</sub> CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH	CN, CO2CH1	CN, CO2CH3	C2Hs CN, CO2CH3	CN, CO2CH3	CH, CN, CO, CH,
TABLE 1 (continued)	R <sub>2</sub>	-CH2CH2N(SO2CH3)CH2CH2-	-CH2CH2-OCH2CH2-	-CH2CH2CH2CH2-	-CH <sub>2</sub> CH <sub>2</sub> N	סיט (	-CH2CH2N ii	й -сн₂сн₂N(с <sub>6</sub> н₅)SO₂CH₃	-CH2CH2OC6H5	CH2CH2N CO-CH2	CH2CH2OC2Hs	CH2CH2OCH2CH2OC2Hs	CH2CH2N COCH-OH	сосн-оссн, си, ј
	RI	-CH 2CH 2	-CH 2 CH	-CH2CH2	C <sub>2</sub> H <sub>5</sub>		C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C2Hs	C <sub>2</sub> H <sub>5</sub>	CH2CH2OC2H5	CH2CH3	CH <sub>2</sub> CH <sub>3</sub>	CH, CH,
	(R) <sub>n</sub>	æ	3-CH3	===	3-CH <sub>3</sub>		3-CH <sub>3</sub>	3-CH <sub>1</sub>	3-CH <sub>3</sub>	3-CH3	æ	3-CH3	3-CH <sub>3</sub>	3-сн,
0 0 0 0 0 0 0	No.	43	44	45	4 6		47	48	49	50	51	52	53	4

	P, Q	CN, CO2CH,	CN, CO <sub>2</sub> CH,	CN, CO2CH,	CN, CO2CH,	CN, CO2CH3	CN, CO2CH3	CN, COOH	CN, CO2CH(CH1)	CO2CH3, CO2CH3	CO <sub>2</sub> CH <sub>3</sub> , CN
TABLE 1 (continued)	R2 COCH,	CH2CH2N CH2CH2	CH2CH2N ii i	C <sub>2</sub> H <sub>5</sub>	CH2CH2CH2SO2CH3	CH2CH2OCOC2H3	-CH2CH=CH2	-CH <sub>2</sub> CH <sub>2</sub> N CO-CH <sub>2</sub>	-CH2CH2N CO-CH2	CH2CH2N II	-CH <sub>2</sub> CH <sub>2</sub> N CO-CH <sub>2</sub>
	R.	CH3	CH2C6H5	CH2C6H11	C <sub>2</sub> H <sub>5</sub>	C2H5	-CH2CH=CH2	-C <sub>2</sub> H <sub>3</sub>	-C <sub>2</sub> H <sub>s</sub>	-C2Hs	-C2H5
	(R) <sub>n</sub>	3-CH3	3-CH <sub>3</sub>	Ŧ	3-CH3	3-CH3	3-CH3	3-сн,	3-CH3	3-CH <sub>3</sub>	3-CH3
Example	NO.	55	56	. 57	28	59	09	61	62	63	64

a Come			TABLE 1 (continued)	
No.	(R) <sub>n</sub>	R	R2	P, Q
65	3-CH3	-C <sub>2</sub> H <sub>5</sub>	-CH2CH2SO2CH=CH2	CO2CH1, CN
99	3-CH <sub>3</sub>	-C2Hs	-CH2CH2SO2CH2CH2SC6Hs	CO2CH3, CN
	i	;		
29	3-CH3	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> CH <sub>2</sub> SC <sub>1</sub>	CO2CH3, CN
89	3-CH3	-C2Hs	-CH <sub>2</sub> CH <sub>2</sub> SC <sub>4</sub> H <sub>9</sub>	CO,CH,, CN
69	3-CH <sub>3</sub>	-C2Hs	-CH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>4</sub> CN)SO <sub>2</sub> CH <sub>3</sub>	CO, CH, CN
70	3~CH3	-C2Hs	-CH2CH2CONH2	CO,CH,, CN
71	3-CH,	-C2Hs	-CH,CH,CON(C,H,),	CO, CH, CN
72	3-CH <sub>3</sub>	-C2Hs	-CH2CH(OCOCH3)CH2OCOCH3 CN, CN	CN, CN
73	3-CH3	-C2H3	-CH2CH2OCC6H5	CN, CN
74	3-CH,	-C2Hs	-ch2ch2occeh11	CN, CN
75	3-CH <sub>3</sub>	-C2Hs	-CH2CH2SO2N(C2H5)2	CN, CO2 CH3
92	3-CH <sub>3</sub>	-C2Hs	-CH2CH2SO2N(CH3)C6H5	CN, CO,CH,
77	3-CH <sub>2</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH2CHS2-CNH	CN, CO2CH,
78	3-CH <sub>3</sub>	-C2Hs	-CH2CH2-S-CN4, OH	CN, CO2CH2C
62	3-CH <sub>1</sub>	-C2Hs	-CH2CH2S-C	CN, CO, CH,

	P, 0	CN, CO2CH3	CN, CO2CH3	CN, CO, CH 3	CN, CO2CH 3	Z-E	CN, -C, Hs	CN, CONHS	CN, CO2CH 3	CeHs, CN	CO <sub>2</sub> CH <sub>3</sub> , CN	CO2CH,, CN
TABLE 1 (continued)	R2	-CH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> -•(-C1	-CH2CH2S-C	-CH <sub>2</sub> CH <sub>2</sub> S-	-сн(сн,)сн,со <sub>2</sub> сн,	-CH(CH1)CH2CO2C2H5	-СН2СН2ОСН2ОН	о -си <sub>2</sub> си <sub>2</sub> осси <sub>2</sub> с <sub>6</sub> и <sub>3</sub>	-CH2CH2OCCH2OCeHs	CH2CH(CeHs)OCCH1	-ch2ch10c0ch31ch2c1 -Ch2ch20ch2c1	-сн,сн,оссн,осн,
	RI	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>s</sub>	-C2Hs	-C2Hs	-C <sub>2</sub> H <sub>\$</sub>	-C <sub>2</sub> H <sub>s</sub>	-C <sub>2</sub> H <sub>5</sub>	-C2Hs	-C2Hs	-C2Hs	-C <sub>2</sub> H <sub>5</sub>
•	(R)	3-сн,	3-сн,	3-CH3	3-CH <sub>3</sub>	3-сн,	3-CH <sub>3</sub>	3-CH <sub>1</sub>	3-CH <sub>3</sub>	3-CH <sub>3</sub>	3-CH <sub>3</sub>	3-сн,
Example.	02	80	81	82	83	8 4	82	98	87	88	06	91

		P, Q	CN, CO, CH,	CN, CO, CH,	CN, CO, CH	CN, CO2CH	CN, CO2CH1	CN, CO1CH1	CN, CO1CH	CN, CO2CH,	CN, CO2CH3	CN, CO2CH3
	29	2	-803-	-80 <sup>3</sup> -	-0-	-CH2CH2-	-020-		*** - \S-\S-	о -осси, си, со-	ос (сн <sub>2</sub> ), со-	O O O O O O O O O O O O O O O O O O O
TABLE 2	(R) 3 = -6 (R)	R 3	-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2O-	-CH2CH2-	-CH2-	-CH 1CH 1-	-CH2CH2-	-CH2CH2-	-CH2CH2-
	P)c=CH	$\frac{R_1}{R_1}$	C <sub>2</sub> H <sub>5</sub>	C2Hs	C2Hs	C <sub>2</sub> H <sub>5</sub>	C2H3	C2Hs	C <sub>2</sub> H <sub>5</sub>	C2H,	C2Hs	C <sub>2</sub> H <sub>5</sub>
		(R) <sub>n</sub>	=	3-CH3	3-CH,	3-CH <sub>3</sub>	3-CH3	3-CH,	3-CH,	3-CH3	3-CH3	3-CH,
		Example No.	92	93	94	95	96	26	86	66	100	101

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	P, Q		CN, CO, CH,	CN, CO2CH,	CN, CO2CH1	CN, CO2CH3	CN, CO2CH3	CN, CN	CN, CN	CN, SO <sub>2</sub> CH <sub>3</sub>	CN, SO2C6Hs	CN, CONHCEHS
	2	- NHC-	-CNH	-02000-	0-10-	-020-	0=0 -	-0C(CH <sub>2</sub> ), CO-	-02	-02	-02	-02
TABLE 2 (continued)	R <sub>3</sub>		-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2OCH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2-
	$\frac{R_1}{I}$		C2Hs	C <sub>2</sub> H <sub>5</sub>	C2Hs	CH2CH2CN	CH2CH2CN	CH2CH2CN	CH2CH2CN	CH2 CH2 CN	CH2CH2CN	си,си,оёси,
	(R) <sub>n</sub>		3-CH <sub>3</sub>	3-CH <sub>3</sub>	æ	æ	Ŧ	=	æ	Ŧ	æ	Ŧ
Example	NO		102	103	104	105	106	107	108	109	110	111

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Example No.	(a)	4	TABLE 2 (continued)		
	(K)	<u>~</u>	R <sub>3</sub>	ы	P, Q
112	2,5-діосн,	C2H5	-CH2CH2-	-02	٥:٠٠ ٢
113	3-C1	C <sub>2</sub> H <sub>5</sub>	-CH 2CH 2-	181	6 CN, CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
114	2-0CH1, 5-C1	C2H5	-CH2CH2-	о -осси,си,си,со-	CN, CO2C2H,CN
115	3-CH,	C <sub>6</sub> H <sub>5</sub>	-CH2CH2-	о -осси,си,со-	CN, CO2CH,
116	3-CH3	C,H11	-CH2CH(CH3)-	о о о о о о о о о о о о о о о о о о о	CN, CO2CH,
117	3-CH3	CH2CH2C6H3	-CH2-		CN, CO2CH3
118	3-CH3	CH2CH2OC2H3	-ch,ch,ch,-	-02	CN, CO2CH,
119	3-сн,	CH2CH2OC6H5	-CH2CH2CH2-	-02	CN, CO2CH3
120	3-си,	CH2CH2N COCH2	-CH2CH2-	-02	CN, -CN,
121	3-сн,	CH2CH2CH3	-CH2CH2-	-02	CN, K
122	3-сн,	СИ,СИ,ОН	-CH 2CH 2-	-805-	CN, CN

	P, 0	CN, CN	CN, CO2CH,	-0-2-5-0-	0 CN C.H3 -0C-C=C-	CO2C2Hs, CO2C2Hs	CO2C2H3, SO2CH3	CN, CeHs	CN, CONH,	COC, H3, COC, H3	CO2C6Hs, CO2C6Hs	CN, CONHC2H, OH	CN, CONHC, H,-n	CN, CONHC&H11	CONH2, CONH2
	ы	-so <sub>2</sub> -	-0¢(cH <sub>2</sub> ),co-	single bond	-00, (CH2), CO-	-0C(CH <sub>2</sub> ), CO-	-0C(CH <sub>2</sub> ),Co-	-0C(CH <sub>2</sub> ),Co-	-00, (CH <sub>2</sub> ), CO-	оо о о о о о о о о о о о о о о о о о о	-00, (CH <sub>2</sub> ), CO-	-02,(cH2),0-	-0C(CH <sub>2</sub> ), CO-	-00 (CH <sub>2</sub> ), Co-	-00, (ch <sub>2</sub> ), co-
TABLE 2 (continued)	R <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> -	-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH <sub>2</sub> CH <sub>2</sub> -	-CH2CH2-	-CH <sub>2</sub> CH <sub>2</sub> -	H, -CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2-	-CH2CH2-
	R1	CH2CO2CH3	CH2CH2C1	C2Hs	C2Hs	C, Hs	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH(CH))CH2CO2CH, -CH2CH2-	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>3</sub>	C2Hs	C2H5	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
	(R) <sub>n</sub>	3-CH,	3-си,	3-CH3	3-CH3	3-CH3	3-сн,	3-CH,	3-CH <sub>3</sub>	3-CH3	3-CH3	3-CH <sub>3</sub>	3-сн,	3-CH,	3-СН3
Example	NO.	123	124	125	126	127	128	129	130	131	132	133	134	135	136

					Ή,						_	2	•
		P 0	CN, CO2CH,	CN, SO,CH,	CO,CH,, CO,CH,	CN, SO2C4Hs	CN, CO2C2Hs	CN, CN	CN, CN	CN, CO2CH,	CN, CONHC, H,	CN, -E	-0"-0"-0"-0"-
			CN,	N U	CO,	S,	N.	CN,	CN	CN	N S	N.	0-0
		R6	CH.	CH.	CH.	CH,	CH.	CH,	CH,	CH.	CH.	CH,	CH.
		Rs	CH 3	CH 3	CH 3	CH,	CH.	CH,	CH.	CH 1	CH,	CH 3	CH,
<b>~</b>		R4, R5	CH, CH,	CH, CH,	CH1, CH1	CH, CH,	CH, CH,	CH3, CH3	CH, CH,	CH1, CH1	CH, CH,	CH3, CH3	CH, CH,
TABLE 3	C=CH-6 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	$R_1$	C2Hs	CH2CH2OH	CH2CH2OH	CH2CH2OH	CH <sub>2</sub> CH <sub>2</sub> OH	C <sub>2</sub> H, OCCH <sub>3</sub>	C2H,OCNH-	C2H,CN	C2H,OH	C <sub>2</sub> H,OH	C2H,OH
		(R) <sub>n</sub>	æ	æ	×	Ŧ	7-CH3	7-CH3	7-CH3	7-CH3	7-CH3	7-CH3	7-CH3
		ample No.	137	138	139	140	141	142	143	144	145	146	147

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	P, Q	SH 3 COOK C. HS	-00	CN, CONHC, H, OH	COC(CH1)11 CN	CN, CO2CH3	CN, CO2C2H5	CN, CONH2	CN, CO2 C6H3	CN, CO2CH,	CN, CO2CH3	CN, CO2C2H,CN	CN, CO2CH3	CN, CN	CN, SO2CH3	CN, CO2CH3	CN, CO2CH3	
	R <sub>6</sub>	į	CH.	CH,	CH3	CH 3	CH.	CH3	CH.	CH,	CH.	CH,	Ŧ	Ŧ	×	<b>=</b>	Ŧ	
(panı	R4, R5	;	CH3 / CH3	CH3, CH3	CH3, CH3	CH3 , CH3	CH3, CH3	CH1, CH1	CH3, CH3	CH, CH,	CH3, CH3	CH3, CH3	H, CH,	H, CH,	H, CH3	H, CH3	н, сн,	
TABLE 3 (continued)	RI		C2H,OH	C <sub>2</sub> H, OH	C2H4OH	C2H, OH	C <sub>2</sub> H, OCC <sub>2</sub> H <sub>5</sub>	C2H, OCC6H,	0 C2H,0C0C2Hs	CH2C6H3	CH2	CH2C4H11	C. H n	CH2CH2OCH2OH	CH2CH2OCCH3	CH2CH2N(C6H5)SO2CH3	 CH2CH2N II	<b>.</b> U= <b>O</b>
	(R)n		7-CH1	7-CH,	7-CH3	<b>=</b>	Ŧ	æ	æ	×	æ	æ	7-CH3	7-CH3	7-CH3	7-CH3	7-CH2	
	No.		148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	

		TABLE 3 (continued)	(pen			
xample No.	(R) <sub>n</sub>	$\mathbb{R}_{1}$	R4, R5	R <sub>6</sub>	OL [	P, 0
163	7-CH3	CH2CH2N CO-CH2	н, сн,	<b>=</b>	CN, C	CN, CO <sub>2</sub> CH <sub>3</sub>
164	7-CH3	CH <sub>2</sub> CH <sub>2</sub> SC S	н, сн,	x	CN, C	CN, CO2CH3
165	5-CH3, 8-CH30	ch <sub>2</sub> ch <sub>2</sub> ch <sub>3</sub>	н, сн,	×	CN,	CN, COACH
166	5,8-di-0CH <sub>1</sub>	сн <sub>2</sub> сн <sub>2</sub> осн <sub>3</sub>	H, CH,	æ	CN	CN, CO2CH,
167	7-0C2H5	он <sub>2</sub> сн <sub>2</sub> оссн <sub>3</sub>	H, CH,	×	CN	CN, CONHC.H.1
168	7-CH3	CH2CH2OCNH-	H, CH,	æ	O= U U:C	
169	7-CH,	CH 2CU 2CH 3	H, CH,	Ŧ	CN C	CN
170	7-CH3	CH2CH2COOH	H, CH,	I	CN,	си, соон
171	7-CH <sub>1</sub>	CH2CH2CON(C2H5)2	H, CH,	x	CONH	CONH2, CO2CH1
172	Ŧ	CH2CH(OH)CH3	H, H	×	CN, CN	CN
173	I	CH2CH(C6H5)OH	H, H	×	CN, CN	CN
174	7-CH3	CeHs	H, CH,	CH 3	CN	CN, CO2CH3
175	7-CH3	CH2CH2S	H, CH,	×	CN	CN, CO2C2H4OH
176	7-CH3	CH2CH2OC6H5	H, CH,	x	CN	CN, CO2C2HC
177	7-CH3	CH2CH2CH2SO2CH3	H, CH,	<b>=</b>	CN	CN, CO2C4H9-1

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	P, Q	CO2C2H5, CO2C2H5	COC, Hs, SO2 CH3	CN, CN	CN, CN	Q CONH2 C6 H5	CN, CO2CH3	CN, CO2CH3	CN, CU2CH1
	R6	CH.	CH 3	CH3	Ξ	×	×	<b>=</b>	×
(þe	R4, R5	CH3, CH3	CH3, CH3	CH3, CH3	CH3, H	CH 3, H	СН, Н	СН,, Н	CH1, H
. TABLE 3 (continued)	$\frac{R_1}{4}$	CH2CH2SO2	CH2	CH <sub>2</sub> CH(OCCH <sub>3</sub> )CH <sub>2</sub> OCCH <sub>3</sub>	СН2СН(ОН)СН2ОН	СН,СН(ОН)СН,ОН	CH2CH=CH2	CH 2 CH 2 N II COOH	Сн <sub>2</sub> Сн <sub>2</sub> N Сн <sub>2</sub> Сн
	(R) <sub>n</sub>	7-Br	7-C1	7-0CH3	7-CH3	7-CH3	7-CH3	7-CH3	7-CH3
Examole	No.	178	179	180	181	182	183	184	185

		P. 0	CN, CN	CN, SO2CH3	CN, SO,C,Hs	CN, CONHC, H,	CN, CONHC2H,OH	CN, CN	CN, SO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH,	CN, CO2CH3	-3=3-30- 0 CN C6Hs
TABLE 4	R R R R	R4	Ξ	Ħ	×	æ	æ	Ξ	æ	æ	3-CH3	3-CH <sub>3</sub>
	C=HC-1	<u>R</u> 1	C2H4OH	C2H4OH	C2H4OH	C2H4OH	C2 H, OH	CH2CH2OCCH3	си, си, осси,	о Си <sub>г</sub> си <sub>г</sub> осси	OH2CH2OC-C6H5	Си, си, осси,
		(R)n	I	æ	Ŧ	æ	x	<b>=</b>	=	6-СИ3	6-СН3	6-CH3
		Example No.	186	187	188	189	190	191	192	193	194	195

	P. 9	-000-	O CONH2 C4 H5	CN, CO2CH1	כא, כא	CN, CO2CH3	CN, CO2CH3	CN, CN	0=1/ /=-	CN, CO2CH,	CN, CO2CH,	CN, CO2CH,	CN, CO2CH,	CN, CO2CH,	CN, CO2CH3
ô	R 4	3-CH3	3~CH3	3-CH1	3-CH3	3-CH3	3-CH3	3-CH	3-CH3	3-CH,	3-CH <sub>3</sub>	3-CH3	3-CH3	3-CH3	3-CH3
TABLE 4 (continued)	R1	CH <sub>2</sub> CH(OH)CH <sub>3</sub>	CH,CH,OCH,CH,OCCH,	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH2	CeHs	CH2	CH2	CH2CH2OCCH3	CH <sub>2</sub> CH <sub>2</sub> CN	CH2CH2N(CH3)SO2CH3	CH2CH2OCNHC6H5	CH2CH2C1	CH2CH2OC6H5	CH2CH2SC6H5
	(R)n	6-CH <sub>3</sub>	6-CH3	6-CH3	6-CH3	6-CH3	6-CH3	6-CH <sub>3</sub>	6-CH <sub>3</sub>	6-CH3	6-CH3	6-CH <sub>3</sub>	€-CH₃	€-CH3	6-CH3
Example	NO.	196	197	198	199	200	201	202	203	204	205	206	207	208	209

·	072	CN, C00H	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO <sub>2</sub> CH <sub>2</sub>	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>	>
<del>(</del>	R4	3-CH3	3-CH 3	3-CH 3	3-CH3	3-CH <sub>3</sub>	
TABLE 4 (continued)	R	CH2CH2S-CS	CH2CH2SO2	CH2CH2N III	-CH2CH2N	-CH <sub>2</sub> CH=CH <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> OC <sub>2</sub> H <sub>4</sub> OH -CH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub> -CH <sub>2</sub> CH(OH)CH <sub>2</sub> OH -CH <sub>2</sub> CH(OH)CH <sub>2</sub> OH -CH <sub>2</sub> CH <sub>2</sub> CON(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> CON(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> CON(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>2</sub> CI	•
	(R)	6-CH3	6-CH3	6-CH3	6-CH3	6-CH <sub>3</sub> 6-CH <sub>3</sub> 6-CH <sub>3</sub> 6-CH <sub>3</sub> 6-CH <sub>3</sub> 6-CH <sub>3</sub>	; ; ;
	Example No.	210	211	212	213	214 215 216 217 218 219 220	777

	P. B	Z-H	CN, -CN	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO <sub>2</sub> CH <sub>3</sub>
inued)	R4	3-CH3	3-CH3	3-CH 3	3-CH <sub>3</sub>	3-CH3
TABLE 4 (continued)	R1	-сн,сн,оёсн,	-Сн <sub>2</sub> Сн <sub>2</sub> оссн <sub>3</sub>	CH2CH2N CH3	о сн <sub>2</sub> сн <sub>2</sub> сн <sub>2</sub> сн <sub>2</sub>	CH2CH2-S-
	(R) <sub>n</sub>	6-CH <sub>3</sub>	6-CH3	6-Сн3	6 – Сн 3	6-CH <sub>3</sub>
e Kamo Jo	No.	223	224	225	226	227

		B . Q	CN, CO2CH3	CN, CO2CH3	CN, CO2C2H5	CN, SO <sub>2</sub> CH <sub>3</sub>	CN, SO2C6Hs	CN, CN		CN, CONHCEHS	-0=0-00-
	0 o	R10	CH,	CeHs	CeHs	C.H.s	C.H.s	CeHs	CeHs	CeHs	CeHs
TABLE 5	S	<u>R</u> 1	CH,	CH,	Ŧ	си, си, осси,	CH2CH2OCCH3	о Си, си, осси,	сн, оссн,	CH, CH, OCCH,	СН2СН2ОН
		<u>R</u> 7	=	æ	æ	×	=	×	æ	æ	Ξ
		Example No.	228	229	230	231	232	233	234	235	236

	P.Q	CN, CONH,	CN	CN, CO2C6H5	CN, CONH2	-00-0 -00-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0	CN, CO <sub>2</sub> CH,	CN, CO2CH2	CN, CO2C2H4OH	CN, CO2CH3	CN, CO2CH,	CN, CO2CH3	CN, CO2CH3	CN, CN	CN, CN	CN, CO2CH3	CN, CO2CH2CH2CN
(pa	<u>R</u> 10	CeHs	CeHs	C <sub>6</sub> H <sub>5</sub>	CeHs	CeHs		Br	- / - CH3	CH,	CH3	CH3	C <sub>6</sub> H <sub>5</sub>	CeHs	C6Hs	CeHs	CeHs
TABLE 5 (continued)	R	CH2CH2OH	СН2СН2ОН	CH, CH, OH	CH <sub>2</sub> CH <sub>2</sub> OH	CH,	CH,	снэ	CH,	CH,	CH3	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH2	CH2	CH2CH2CN	CH2CH2CONH2
	<u>R</u> 7	Ŧ	æ	==	: <b>=</b>	æ	Ŧ	æ	Ŧ	5-CH3	5-C1	5-0CH,	=	Ŧ	×	æ	<b>=</b>
	Example No.	237	238	230	240	241	242	243	244	245	246	24.2	248	249	250	251	252

	P. Q	CN, CO, CH,	CN, CO, CH,	CN, CO, CH,	CN, CO, CH,	CN, CO2CH,	CO <sub>2</sub> CH <sub>3</sub> , -C-1	H CN, COOH	CN, CO, CH, C, H	CN, CO, CH, C, H, 1	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH3	CN, CO2CH,	CN, CO2CH3
(per	R10	CeHs	CeHs	CeHs	C <sub>6</sub> H <sub>5</sub>	 <b>x</b>	=	Ŧ	CeHs	C 6 H 4 - P-COOH	C6H4-P-CO2CH3	C <sub>6</sub> H <sub>5</sub>	C 6 H 5	CeHs
TABLE 5 (continued)	R1	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCC <sub>6</sub> H <sub>5</sub>	CH2CH2CH2NHSO2C6H5	CH2CH2CH2N(CH3)SO2CH3	CH2CH2CH2N(C2H,OH)SO2CH3	CH <sub>3</sub>	снэ	CH <sub>3</sub>	CH,	CH,	C <sub>t</sub> H <sub>9</sub> -n	CH2CH2N II	CH2CH2N COCH2	CH2CH2CH2N C-CH2
	R <sub>7</sub>	æ	<b>=</b>	æ	=	æ	æ	Ŧ	I	æ	=	×	=	==
Example	NO.	253	254	255	256	257	258	250	260	261	262	263	264	265

	B 7 G	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>
nued)	<u>R</u> 10	C&Hs	CeHs	CeHs
TABLE 5 (continued)	<u>R1</u> O	CH2CH2CH2N	CH2CH2CH2N CH2CH2CH2N	C 6 H 5
	R. 1	×	×	æ
	Example No.	266	267	268

		TABLE 6	9	
		P C=HC	S R R	
Sxample No.	<u>R</u> 8	<u>R</u> 9	R10	P . Q
269	CH,	CH 3	CH,	CN, CO, CH3
270	CH3	CH,	CH,	CN, CO2C2HS
271	CH3	CH,	CaHs	CN, CO2CH3
272	CH.	CH3	CeHs	CN, CUOH
273	CH3	CH,	CeHs	CO2C2Hs, CO2C2Hs
274	CH3	CH3	CeHs	CN, CONHC2H,OH
275	CH.	CH 2 CH 2 OH	CeHs	CN, CN
276	CH3	CH2CH2OH	C <sub>6</sub> H <sub>5</sub>	CN, SO2CH2
277	CH.	CH2CH2OH	CeHs	CN, SO2C6H5
278	CH.	CH2CH2OH	CeHs	CN, CONHC&H5
279	CH3	CH2 CH2 OH	CeHs	مياً له
280	CH <sub>3</sub>	CH2CH2OH	CeHs	0 CN Ç, H,5 0 CN Ç, H,5 0 CN Ç, H,5

	P. 2	CN, CN	CN, CN	CN, CO2CH3	CN, CO2CH2CH2CN	GN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH3	CN, CN		-CN, -CN,	-CN, -CN,
TABLE 6 (continued)	R10	CeHs	CeHs	C.H.s	CeHs	CeHs	C <sub>6</sub> H <sub>5</sub>	CeHs	C <sub>6</sub> H <sub>5</sub>	æ	C <sub>6</sub> H <sub>3</sub>	CeHs
	(원) (건	сн,сн,ойсн,	CH2CH2OCOC2H3	CzHs	CeHs	· · · · · · · · · · · · · · · · · · ·	CH <sub>3</sub>	, , , , , , , , , , , , , , , , , , ,	// \	CH3		
	<u>R</u> 8	CH,	CH,	C2Hs	C2H5	C2Hs	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH2CH2OH	СН3	СН2СН2ОН	CH2CH2OH
Example	NO.	281	282	283	284	285	286	287	288	289	290	291

	P. 9	CN, -C	CN, SO <sub>2</sub> (H <sub>1</sub>	CN, SO <sub>2</sub> ,-C1	CN, SO <sub>2</sub> ,	CN, CO2CH3	CN, CO2CH1	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>				
TABLE 6 (continued)	R10	CeHs	CeHs	CeHs	CeHs	CeHs	CeHs	CeHs	CeHs				. Br
	<u>R</u> 9				ii	CH 2 C 6 H 3	CH2 C6 H5	CeHii	C, H9-n	сн	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CeHs
	R8	CH <sub>2</sub> CH <sub>2</sub> OH	СН2СН2ОН	CH2CH2OH	CH2 CH2 OH	CH.	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH,	C, H, n	CH <sup>3</sup>	CH.	CH3	CH3
	Example No.	292	293	294	295	296	297	298	299	300	301	302	303

	P. Q	2 —— 2-20- 5 —— 2-20-	о созснэ сенз
ABLE 6 (continued)	R10		
TABLE 6	<u>R</u> 9	CeH s	C6Hs
	R	СН3	C, H9-n
	Example No.	304	305

		P. Q	CN, CO, CH,	CN, CO, CH, CH, CN	CN, CO,CH,CH,OH	"O'HO'HO'O' 'NO		CN CO2CH2C6H11	CO2C2Hs, CO2C2Hs	COOH, CN	-0-с-с	CN, CO,CH,	CN, CO, CH,	CN. CO.CH.	Tan Co No	CIV. CO2CII3	CN, CN
E 7	s 6 6 7(R)	R12	Ŧ	E	Ŧ	×	: =	2 :	<del></del>	<b>X</b>	¥	Ŧ	æ	=	: #	:	<b>=</b>
TABLE 7	RIZA SILIA SILIA SILIA	R11	×	×	<b>32</b> 3	æ	==	: =	e	=	×	Ŧ	Ŧ	Ŧ	=	: 3	<b>.</b>
		(R) <sub>n</sub>	<b>±</b>	×	æ	Ŧ	<b>*</b>	<b>a</b>	: :	æ	x	5-CH <sub>3</sub>	5-0CH3	5-01	5,7-di-CH,	. no-y	ט-ניים
	•	Example No.	306	307	308	309	310	311	31.2	777	313	314	315	316	317	318	) 1

	9 4 0	•=•	CN, CN,	CN, THE	CN, SO <sub>2</sub>	CN, SO <sub>2</sub> ,C1	CN, C6Hs	- 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0	CN, CN	CN, CO2CH3	CN, CO2CH3
	R12	<b>±</b>	æ	Ŧ	Ŧ	æ	×	æ	Œ	Ŧ	<b>z</b> .
TABLE 7 (continued)	<u>R</u> 11	. НО	но	ОН	НО	НО	Ю	Ю	ococ2Hs	OCC.Hs	оесн,с1
	(R) <sub>n</sub>	5-CH <sub>3</sub>	5-CH3	5-CH3	5-CH3	5-CH <sub>3</sub>	5-CH3	5-CH3	5-CH <sub>3</sub>	5-CH <sub>3</sub>	5-CH3
•	Example No.	319	320	321	322	323	324	325	326	327	328

	P. 2	CN, CN	CN, CN	CN, CO2CH3	CN, CO2CH,	CN, CO2CH3	CN, -KNJ	CN, -R-1	CN, 1 - OCH,	CN, CH,	CN, CN	CN, CO2CH3	CN, NO2	CN, ( CO <sub>2</sub> CH,
	R12	ю ч	OCCH,	T	CH,	<b>=</b>	±	I	¥	<b>=</b>	Ŧ	¥	Ŧ	×
TABLE 7 (continued)	<u>R</u> 11	НО	ойсн,	CH,	CH 3	OCNHC & H s	осси,	осси, ос <sub>е</sub> и,	0 6 6 6 7 8 9	осинс <sub>2</sub> н <sub>5</sub>	, - 50 S50		осн <b>,</b>	о ОССН <b>,</b>
	(R)	×	æ	×	æ	Ŧ	Ŧ	±	<b>=</b>	æ	<b>=</b>	<b>=</b>	±	Ξ
SX3mm)	No.	329	330	331	332	333	334	335	336	337	338	339	340	341

		P. Q	CN, CO2CH3	CO2CH2CH3, CO2CH2CH3	CO2CH1, SO2CH1	CO2CH3, SO2C6H3	CN, CONHC, H, OH	CN, CO2CH2CH2OH	CN, CO2CH2CH2OC2H5	CN, CO2CH2CH2C1	CN, CO2CH2CH2C6H5	CN, CO2CH2CH2OC6H5	CN, CO2C6H5	CN, CO2C6H11	CN, CO2CH2C6H11	CN, CO2CH2C6H5	CN, CO2CH2CH(CH1)2
TABLE 8	s CH <sub>3</sub> s I I CH-CH <sub>3</sub> R <sub>7</sub> N CH-CH=(	R7	æ	. <b>.</b>	<b>=</b>	Ŧ	£	Ŧ	H	I	£	x	×	I	æ	Ŧ	5-CH <sub>3</sub>
		Example No.	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356

	P. 2	CN, CO2CH2CH2CN	CN, CO2CH2	CN, CN	CN, CO2CH3	CN, COOH	CN, CONHC&H5	CN, CONHC2H5	CN, SO2CH,	CN, SO2C4Hs	CN, COC(CH <sub>3</sub> ) <sub>3</sub>	0:0/	=• • \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	0 CN C. Hs	-0°-c°-c°-c°-c°-c°-c°-c°-c°-c°-c°-c°-c°-c°	CN, -K-III	Z-x NO
TABLE 8 (continued)	R7	5~0CH <sub>3</sub>	5-C1	5-C00H	5-C00H	5-соон	5-C00H	5-COOH	5-соон	5-C00H	5-C0 <sub>2</sub> CH <sub>3</sub>		5-CO <sub>2</sub> CH <sub>3</sub>	5-CO <sub>2</sub> CH <sub>3</sub>	5-C0 <sub>2</sub> CH <sub>3</sub>	5-CO <sub>2</sub> CH <sub>3</sub>	5-C0 <sub>2</sub> CH <sub>3</sub>
, אל משראק מן משראק	NO.	357	358	359	360	361	362	363	364	365	366		367	368	369	370	371

	12 2.4	CN, SO <sub>2</sub> (-C1	CN, CO2C2Hs	CN, CO2CH1	CN, CO2CH3	CN, CN	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH,	CN, C00H	0 C00H CeHs	0 CONH 2 C6H 5 OC-C====C-	CO <sub>2</sub> CH <sub>3</sub> , -C <sub>1</sub>	CN, -K	CN, CONH
TABLE 8 (continued)	R <sub>7</sub>	5-со,сн,	5-C02CH2CH3	5-CO2CH2C6H3	5-CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	5-CO2CH2CH4	5-CO2CH2CH2CN	5-CO <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	S-C00H	S-C00H	5-C00H	5-C00H	5-C00H	5-соон
e van 1e	No.	372	373	374	375	376	377	378	379	380	381	382	383	384

		D 74	CN, CO2C1Hs	CN, CO2C2H,OH	CN, CO2CH1	CN, CO2CH1	CN, CO2CH2CH2CN	CN, CO2CH2CH2OCH3	CN, CO2CeHs	CN, CO2CH2CH2C6H3	CN, CO2CH2CH2OC6H5	CN, CONHC, H, OH	CN, CO2CH3	CN, CO2CH3	CN, CO2CH3	CO2C2Hs, CO2C2Hs	CN, CO, CH,
	-CH=CH-CH=C	R2	CH,	CH.	CH3	CH3	CH.	C2Hs	C2Hs	C2Hs	C.H. J.	C2H3	C2Hs	C2H5	CeHs	CeHs	=
TABLE 9	$R_1 = \begin{cases} R_1 & R_2 \\ R_1 & R_3 \\ R_1 & R_4 \end{cases}$	<u>R</u> 1	CH <sub>3</sub>	CH,	CH3	CH,	CH,	C2Hs	C2Hs	C <sub>2</sub> H <sub>5</sub>	C.H9-n	CH2CH(CH3)2	C6Hs	C <sub>6</sub> H <sub>5</sub>	CeHs	C <sub>6</sub> H <sub>5</sub>	;
		(R)n	#	=	3-CH3	3-0C2Hs	3-61	2-0CH3, 5-CH3	2,5-di-OCH,	2,5-di-CH,	3-CH3	3-C2H3	=	3-0CH3	<b>5</b>	<b>=</b>	
		Example No.	385	386	387	388	389	390	391	392	393	394	395	396	397	398	,

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	P, Q	CN, CO2CH3	CN, CN	CN, CN	CN, SO2CH3	CN, -R	-0C-C-C-C-C-C-	CN, CO2CH3	CN, CO2CH3	CN, CN	0:2/ 1/20	) = ·	• ;=0
nued)	<u>R</u> 2	CH <sub>2</sub> ,	CH <sub>2</sub> , COOH	CH2	CH1	C <sub>2</sub> H <sub>5</sub>	CH 2	CH2CH2C1	C2H5	CH2CH2OH	CH2CH2OH	си,си,осси,	
TABLE 9 (continued)	. R1	CH2	CH <sub>2</sub> (-C00H	CH2	CH <sub>2</sub> (	CH2	CH 2-	CH2CH2C1	CH2CH2OC2H4OC2H5	CH2CH2OH	CH2CH2OH	сн, сн, оссн,	
	( <u>R)</u> n	æ	Ŧ	Ŧ	Ŧ	×	3-CH3	. 3-CH3	3-CH3	3-CH <sub>3</sub>	3-сн,	3-CH <sub>3</sub>	
Example	No.	400	401	402	403	404	405	406	407	408	409	410	

	D 14	NO NO	CN, CN	CN, SO2CH3	CN, SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CN, SO2C6H11	CN, CN	CN, CN	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, SO <sub>2</sub> 61	CN, -LN	CN, CO2CH3	GN, CN	CN, CO2CH2
(pe	<u>R</u> 2	ch, ch, occh,	C2Hs	CzHs	C2Hs	C2Hs	CH2CH2OCOC2H3	CH2CH2OCOC2H3	CH2CH2OCNH	CH2CH2OCC2H3	си,си,осс,и,	Сн, сн, ос.	CH2CH2OCCH2	СН,
TABLE 9 (continued)	<u>R</u> 1	ch,ch,oëch,	CH 2CH (OH) CH 2OH	CH2CH(OH)CH2OH	о о о о о о о о о о о о о о о о о о о	CH <sub>2</sub> CH(OH)CH <sub>3</sub>	Снгосости	CH2CH2OCC6H3	CH2CH2OCNH-	CH <sub>2</sub> CH <sub>2</sub> OCC <sub>2</sub> H <sub>5</sub>	0 0 0 0 0 0 0 0	сн, сн, ос-	CH2CH2OCCH2	CH <sub>3</sub>
	(R)n	3-CH <sub>3</sub>	3-CH <sub>1</sub>	3-CH3	3-CH,	3-CH3	3-CH3	3-CH,	3-CH3	3-CH,	3-CH <sub>3</sub>	3-CH3	3-CH1	3-CH3
	Example No.	411	412	413	414	415	416	417	418	419	420	421	422	423

	·	P. 9	CN, CO2CH,	CN, CO2C2H,OH	CN, CONHC2H4OH	CN, CO2CH2CH2CN	CN, CO2CH2CH2OC2H5	CN, CO2CH2CH2C6H5	CN, CO2CH2C6H3	CN, CO2CH2CH2OC4H5	CN, CU2C2HS	CO2C2Hs, CO2C2Hs	CO2CH1, SO2CH1	CN, CN	CN, SO2C&H5
		$\frac{R}{6}$	CH 3	CH,	CH,	CH,	CH 3	CH.	CH3	CH,	CH.	CH.	CH.	CH 3	CHJ.
TABLE 10	R-N-R	R41. R5	CH3, CH3	CH1, CH1	CH3, CH3	CH1, CH1	CH1, CH1	CH3, CH3	CH3, CH3	CH, CH,	CH3, CH3	CH3, CH3	CH3, CH3	CH1, CH1	CH, CH,
	C=HC-1	<u>R</u> 1	CH <sub>3</sub>	CH,	CH,	CH3	CH3	CH3	CH1	CH,	CH2CH2C1	CH2CH2OH	CH2CH2OCeH5	°нээо*нэ*нэ	си, си, оёси,
	,	(R)n	æ	×	æ	×	×	Ħ	æ	æ	I	æ	æ	Ŧ	<b>=</b>
		Example No.	424	425	426	427	428	429	430	431	432	4.33	434	435	436

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	R6 P. Q	CH <sub>3</sub> CN, SO <sub>2</sub> CH <sub>3</sub>	CH, CONHC&Hs	CH3 CN, CONHC2H4OH	H CN, SO <sub>2</sub> CH <sub>3</sub>	C.H3 CN, CO2CH3	CH, CH,	CH, CONH	CH, -0C-CH,	CH <sub>3</sub> -0C-C -C -C-C	сн, состобно сень сень сень сень сень сень сень сень	CH3 CN, CO2CH3	
TABLE 10 (continued)	R41_R5	CH, CH,	CH, CH,	СН , Н	H , H	н, н	H .	H .H	# 1	Н, Н	н, н	н <b>н</b>	:
TABLE 10	RI	cH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub>	сн, сн, оёсн,	CH2CH2OCCH3	CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub>	сн, сн, оссн,	сн, сн, оссн,	CH, CH, OCCH,	CH 2 CH 2 OC OC 2 H 5	CH, CH, OCC, HS	CH2CH2OCNH-	CH2CH2CH2NHC-	וט־אט־אט
	(R)n	æ	×	¥	æ	<b>=</b>	6-C1	7-CH <sub>3</sub>	æ	z	æ	æ	=
Examp]e	NO.	437	438	439	440	. 441	442	443	444	445	446	447	448

	P. Q	CN, CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CN, CO2CH2C6H5	CN, CN	CN, CN	CN, -C,	CN, TIN	Z-E Z-E	CN, SO <sub>2</sub> C1	CN, CO2CH,	CN, CO2CH2CH2CN
	<u>R</u> 6	CH,	CH3	CH 3	CH,	CH.	СН	CH.	CH <sub>1</sub>	CH.	CH.
tinued)	R41_R5	H , H	# <b>*</b>	H, H	H, H	H .H	H .	н ,	н, н	H .H	# '#
TABLE 10 (continued)	R1	ž	CH2	CH2	CH2	CH2	CH2	CH2	CH2	C <sub>6</sub> H <sub>5</sub>	CH2CH2OCCH2C6H3
	(R)n	<b>x</b>	æ	<b>=</b>	æ	æ	æ	æ	æ	Ŧ	æ
of case of	No.	449	450	451	452	453	454	455	456	457	458

	P. Q	CN, COC(CH1)2	CN, COC&HS	си, соон	CN, CeHs	CN, , NO	CN,
	<u>R</u> 6	CH,	CH.	CH 3	CH,	CH.	CH.
TABLE 10 (continued)	R41 R5	H , H	H 'H	H 'H	# #	H , H	н 'н
TAE	<u>R</u>	CH2 CH2 OCCH3	сн, сн, оссн,	CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub>	сн, сн, оссн
	(R)n	Ŧ	æ	x	×	Ŧ	Ŧ
	Example No.	459	460	461	462	463	464

		P. Q	CN, CN	CN, CONH2	CN, CO2CH,	CN, CONHC&H5	٥٠٠٧	=• \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	CN, CN	CN, CO2CH3	CN, SO2CH3	CN, SO2CeHs
TABLE 11	$\begin{cases} R_1 \\ R_2 \\ R_1 \end{cases}$	RI	CH 2CH 2OH	CH 2CH 2OH	CH 2 CH 2 OH	CH 2 CH 2 OH		CH <sub>2</sub> CH <sub>2</sub> OH	CH2CH2OCCH3	сн 2 сн 2 оски 3	ch <sub>2</sub> ch <sub>2</sub> och <sub>3</sub>	ch <sub>2</sub> ch <sub>2</sub> ch <sub>3</sub>
I	C=HC-1	(R.)n	×	æ	æ	. 32		Ŧ	æ	æ	±	Ŧ
		<u>(R)</u> n	Ŧ	35	×	<b>3</b> 2		=	Ŧ	æ	æ	Ŧ
		Example No.	465.	466	467	468		469	470	471	472	473

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	P. Q. 1	CN, -CN,	-2=2-20- 5 H 3 N 5 0		CN, COC, Hs	CN, COC(CH1)1	CN, C <sub>8</sub> H <sub>4</sub>	CN, CO, CH,	CN, CO, CH,	CN, CO2CH3	CN, CU2CH,	CO2C2Hs, CO2C2Hs	-33-30- 0 CN CeHs	CN, CN	CN, CN
TABLE 11 (continued)	. <u>R</u> 1	сн,сн,оёсн,	CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub>	CH2CH2OCCH3	си,си,оёси,	CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub>	CH2CH2OCOC2H3	CH2CH2C1	CH2CH2OH	C <sub>2</sub> H <sub>s</sub>	CH <sub>2</sub>	CH <sub>3</sub>	сн 2СН (ОН )СН 3	CH2	CH2
TABLE	(R')n	æ	x	æ	Ŧ	æ	π	æ	<b>T</b>	T	æ	Ŧ	×	Ŧ	T
	(R)n	×	×	<b>=</b>	<b>=</b>	<b>=</b>	æ	¥	3-CH3	3-CH3	3-CH3	Ŧ	×	×	æ
Example	No.	474	475	476	477	478	479	480	481	482	483	484	485	486	487

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	P. Q	CN, CONH2	CN, CO2CH2CH2CN	CN, CO2CH2CH2OC2H5	CN, CN	CN, SO <sub>2</sub>	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH,	CN, CO2CH3	CN, CO2CH3	CN, CO2CH3	CN, CO2CH3	CN, CO2CH,	CN, CO2CH1		CN, CO2CH3
TABLE 11 (continued)	R.	CH2	CH2 CO2 CH3	CH <sub>2</sub>	CH <sub>2</sub>	CH2	сн,	CH,	C2H5	CH2CH(CH3)2	CH2C6H5	CH2CH2SO2C6H5	CH2CH2CN	CH2CH2OC6H5	<u>"</u>	CH2CH2S-K
TABLE 1	IR'In	×	3'-CH <sub>3</sub>	2,-CH,	3'-0CH <sub>3</sub>	Ŧ	=	3'-CH3	×	Ŧ	Ŧ	æ	×	æ		×
	( <u>R)</u>	Ŧ	3-CH3	3-013	3-CH,	2,5-di-OCH3	2,5-di-CH,	3-Br		Ŧ	Ŧ	Ŧ	x	æ		æ
•	Example No.	488	489	490	491	492	493	494	495	496	497	498	499	200		501

	D 7 d	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH3	CN, CO2CH3	-2=== 2-20- °0-с-с-с-с-	CN, CO2CH2CH2OH	CN, CONHC, H, OH
TABLE 11 (continued)		CH <sub>2</sub> CH <sub>2</sub> N <sub>2</sub> H <sub>2</sub> CH <sub></sub>	CH <sub>2</sub> CH <sub>2</sub> -N	CH <sub>2</sub> CH <sub>2</sub> N SO <sub>2</sub> -	CH2CH2SO2NH	CH 2 - CH	CH2	CH <sub>2</sub> C <sub>1</sub>
TABLE 1	(R')n	<b>#</b>	<b>=</b>	<b>x</b>	±	æ	Ξ	±
	<u>(R)</u> n	±	Ŧ		<b>=</b>	Ŧ	x	<b>=</b>
Example	NO.	502	503	504	205	206	507	208

		요1	C	C	CN	CO2CH1	CO <sub>2</sub> CH <sub>3</sub>	CO2CH3	CONH 2
7	P	(R)n	Œ	Ŧ	æ	<b>*</b>	<b>=</b>	, 2-CH,	2-C1
TABLE 12	A-CH=C-* (R)	<b>∢i</b> 	(HOC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> N	(CH <sub>3</sub> COC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> N(CH <sub>3</sub>	CH, COCH, CH2		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	NCCH <sub>2</sub> CH <sub>2</sub> N-* CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>2</sub> N-*
		Example No.	509	510	511	512	513	514	515

	<u>م</u> ا	N C	CN	N.	CN	CN	CS
	( <u>R)</u> n	±	2,5-di-CH,	<b>₹</b>	Ŧ	æ	2-0CH <sub>3</sub>
TABLE 12 (continued)	A CH,		CH <sub>3</sub> CH <sub>3</sub> ) 2 CH <sub>3</sub> CH <sub>3</sub> CCH <sub>3</sub>	сн, оссн, о	CH3-1   CH2-1-CO2CH3	C. H 5 C. H. OH	1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
Example	NO.	> 516	517	518	519	520	521

	ᆈ	CO2CH3	CO2CH3	CN	CN	N	N C
	(R)n	Ξ	æ	æ	H #	æ	<b>x</b>
TABLE 12 (continued)	۷I	S CH <sub>3</sub>	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	(HOC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> N("CH=CH-	(CH <sub>3</sub> COC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> N(	CH <sub>3</sub> CH <sub>4</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>4</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>4</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>4</sub> CH <sub>4</sub> CH <sub>4</sub> CH <sub>4</sub> CH <sub>3</sub> CH <sub>4</sub>	C2H, OCCH
Examp]e	No.	522	523	524	525	526	527

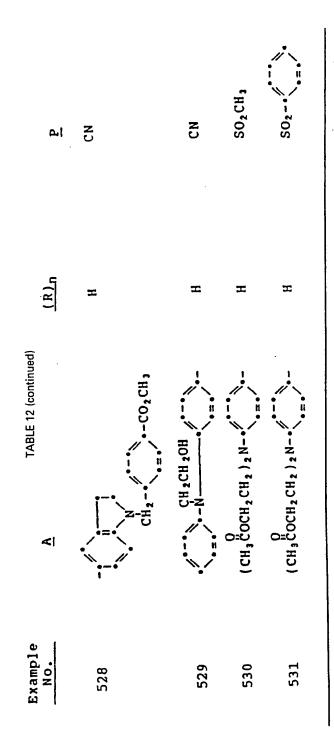


		TABLE 13	
		$Q = HC - \frac{7}{1} \qquad \qquad$	
Example No.	( <u>R)</u> n	<u>R</u> 1	P. 2
532	×	C <sub>2</sub> H <sub>4</sub> OH	CN, CN
533	I	C2H,OH	CN, SO2CH3
534	×	C <sub>2</sub> H, OH	CN, SO2C6H5
535	æ	C2H,OH	CN, CONHCeH5
536	×	C2H, OH	CN, CONHC2H4OH
537	Ŧ	сн2сн2оссн3	CN, CN
538	æ	CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub>	CN, SO <sub>2</sub> CH <sub>3</sub>
539	4,8-di-CH3	CH2CH2OCCH3	CN, CO2CH,
540	8-CH3	CH2CH2OC-C6H3	CN, CO <sub>2</sub> CH <sub>3</sub>
541	8 – CH 3	CH2CH2OCCH3	-0C-C=C-C6Hs
542	8-CH3	CH <sub>2</sub> CH(OH)CH <sub>3</sub>	-0=-2-20- 0 coon ce 43

P. Q. CONH, C. H.	-0 <u>c</u> - <u>c</u> - <u>-0</u> -	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CN	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CN	) = 1 	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>
TABLE 13 (continued) $\dfrac{R_1}{O}$	сн 2сн 2сн 2сн 20 ёсн 3	НООО	CH2	CeHs	CH2	CH2	си, си, оёсн,	()C02CH3	CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> )SO <sub>2</sub> CH <sub>3</sub>	CH2CH2OCNHC6H5	CH2CH2C1	CH2CH2OC6H5	CH2CH2SC6H5
<u>(R)</u> n	2-C1-8-CH3	4-C1-8-CH3	8-CH3	8-CH3	æ	4-OCH3-8-CH3	3,4-di-Cl-8-CH3	Ŧ	æ	6,8-di-CH3	6,9-di-CH <sub>1</sub>	8-CH3	8 -CH3
Example No.	543	544	545	546	547	548	549	550	551	552	553	554	555

	P, Q	CN, C00H	CN, CO2CH3	CN, CO <sub>2</sub> CH,	CN, CO2CH3	CN, CO2CH3	CN, CN	CN, CO2CH3	CN, COC(CH <sub>3</sub> ) <sub>2</sub>	CN, CO2CH3	CN, CO, CH3	CN, CO2CH3	CN, CO2CH3	CN, -CN
TABLE 13 (continued)	R1	CH2CH2S-US	CH2CH2SO2	CH2CH2N	-CH2CH2N	-CH2CH=CH2	-CH2CH2OC2H4OH	-CH2CH2SO2CH=CH2	-CH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	-CH2C6H11	-CH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	-CH2CH2CON(CH3)C6H5	-CH2CH2OCCH2C1	-сн2сн2оёсн3
	<u>(R)</u> n	4-0CH3-8-CH3	8 CH 3	8 - CH 3	8-CH <sub>3</sub>	8-CH3	8-CH3	8-CH <sub>3</sub>	8-CH <sub>3</sub>	9-CH <sub>3</sub>	9-CH <sub>3</sub>	9-CH <sub>3</sub>	4-CH3	4-CH <sub>3</sub>
Example	NO.	556	557	558	559	260	561	295	263	564	265	266	267	568

P. Q	Z-T	C N N N N N N N N N N N N N N N N N N N	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>
TABLE 13 (continued) $rac{R}{1}$	о -сн <sub>2</sub> сн <sub>2</sub> оссн <sub>3</sub>	о -сн <sub>2</sub> сн <sub>2</sub> оссн <sub>3</sub>	$CH_2CH_2N$ $CH_2CH_2$ $CH_2CH_2$	CH2CH2N G-CH2	CH2CH2-S-
(R.)n	4 - CH <sub>3</sub>	4-CH,	2-CH <sub>3</sub> , 8-OCH <sub>3</sub>	4,8-di-OCH3	6,9-di-CH3
Example No.	569	570	571	572	573

		TABLE 14	
		$Q = HC - \begin{cases} & & & & & & & \\ & & & & & \\ & & & & &$	
Example No.	( <u>R)</u> n	R1	Q 49
574	Ŧ	C <sub>2</sub> H <sub>4</sub> OH	CN, CN
575	æ	C <sub>2</sub> H <sub>4</sub> OH	CN, SO2CH3
929	Œ	HOOD	CN, SO2C6H5
577	æ	CH2	CN, CONHC&HS
578	Ŧ	C <sub>2</sub> H <sub>4</sub> OH	CN, CONHC2H,OH
579	æ	сн2сн2оссн3	CN, CN
580	×	сн2сн2оссн3	CN, SO2CH3
581	8 -CH3	CH2CH2OCCH3	CN, CO2CH3
582	8 -CH3	CH2CH2OC+C6H5	CN, CO2CH3

,	P. Q. C. H.	-0	-0C-C-C-C-C-	0 CUNH2 C6 H5	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CN	CN, CO2CH3	CN, CO2CH3	CN, CN	0::0	CN, CO2CH3	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO <sub>2</sub> CH <sub>3</sub>
TABLE 14 (continued)	<u>R</u> 1	CH2CH2OCCH3	CH,CH(OH)CH,	CH 2CH 2CH 2CH 3	HOOD	CH2	CeHs	CH2	CH2{}-COC1	снгосснз	нооо-	CH2CH2N(CH3)SO2CH3	CH2CH2OCNHC6H5
71	(R)n	8-CH3	, I	2-C1-8-CH <sub>3</sub>	4-C1-8-CH3	5,8-di-CH3	æ	Ŧ	æ	3-CH3	3-CH3	3-CH3	3-0CH <sub>3</sub> -8-CH <sub>3</sub>
	No.	583	, y	585	586	587	588	589	590	591	592	593	594

P 49	CN, CO <sub>2</sub> CH <sub>3</sub> CN, CO <sub>2</sub> CH <sub>3</sub> CN, CO <sub>2</sub> CH <sub>3</sub>	CN, COOH	CN, CO2CH3	CN, CO2CH3	CN, CO2CH3	CN, CO2CH3	CN, COC(CH <sub>3</sub> ) CN, CO <sub>2</sub> CH <sub>3</sub> CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH3
TABLE 14 (continued) R1	CH2CH2C1 CH2CH2OC6Hs CH2CH2SC6Hs	CH2CH2S-CS-N-1	CH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> (H <sub>3</sub> )	CH <sub>2</sub> CH <sub>2</sub> N ii ii	-CH2CH2N ii	-CH <sub>2</sub> CH=CH <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> OC <sub>2</sub> H <sub>4</sub> OH	-CH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub> -CH <sub>2</sub> CH(OH)CH <sub>2</sub> OH -CH <sub>2</sub> C <sub>6</sub> H <sub>11</sub> -CH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	-CH2CH2CON(CH3)CeHs
(R)n	3-0CH <sub>3</sub> -7-CH <sub>3</sub> 3-0CH <sub>3</sub> -7-CH <sub>3</sub> 3-0CH <sub>3</sub> -7-CH <sub>3</sub>	3,5-di-CH,	3,5-di-CH <sub>3</sub>	3-0CH3	7,10-di-CH3	3,8-di-CH <sub>3</sub>	8-CH <sub>3</sub> 8-CH <sub>3</sub> 8-CH <sub>3</sub>	8-CH <sub>3</sub>
Example No.	595 596 597	598	599	009	601	602	604 605 606	809

P. 4.9	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, -C	CN, THE THE TENT	CN, -CS	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO <sub>2</sub> CH <sub>3</sub>	CN, CO2CH3
TABLE 14 (continued) R1	о -сн,сн,оёсн,с1	-сн2сн2оссн3	-CH2CH2OCCH3	о -сн <sub>2</sub> сн <sub>2</sub> оёсн <sub>3</sub> 0	CH <sub>2</sub> CH <sub>2</sub> N CH <sub>3</sub>	СН <sub>2</sub> СН <sub>2</sub> СН <sub>2</sub> СН <sub>2</sub>	CH2CH2-S-IN
(R)n	<b>±</b>	æ	æ	5,8-di-CH3	5,8-di-CH3	8-CH3	7,9-di-OCH3
Example No.	609	610	611	612	613	614	615

$$\frac{P_{f} Q}{CN_{f} CO_{2}CH_{3}}$$
 $\frac{Q}{Q} \frac{COOH}{C} C_{6}^{6}H_{5}$ 
 $\frac{Q}{CO_{2}CH_{3}}, CO_{2}CH_{3}$ 
 $CO_{2}CH_{3}, CO_{2}CH_{3}$ 
 $CN_{f} CO_{2}CH_{2}CH_{2}OH$ 

TABLE 15

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	0 'd	2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 -	O CO2CH3 C6H5	CN, CONHC2H,OH	O CN C6 H5	CN, CO2CH3	CN, SO2	0 CO2CH3 C6H3	0 со2сн3 сен3 -ос-с===с
TABLE 15 (continued)	<b>m</b>	HJ S	HU-S		HOOD-	-N II-SC <sub>2</sub> H <sub>5</sub>	-N-C-CH <sub>3</sub>	CH <sub>3</sub>	
	(R)10	C& H, -p-CO2CH3	C & H & - P - C O O H	C <sub>6</sub> H <sub>4</sub> -p-Br	C <sub>6</sub> H <sub>4</sub> - p-0CH <sub>3</sub>	CeHp-CH3	C&H&-0-C1	C & H 4 - m - CO 2 CH 3	C&H&-P-CO2CH3
	Example No.	621	622	623	624	625	979	627	. 628

CN, CO2CH3	CN, CONHC, H, OH	0=0	CN, CO2CH3	CN, CONH	O CN C6 H5	O CN C6 Hs	CN,
TABLE 15 (continued)  B  -N  II-S-C <sub>2</sub> H, OH	-N 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0			)=-  =-  Z-=	-çcH <sub>3</sub>	-N- -II- S	-N- -II- SSSSCO <sub>2</sub> CH <sub>3</sub>
(R) <u>10</u> CeHs	C e H s	C <sub>6</sub> H <sub>5</sub>	CeHs	C <sub>6</sub> H <sub>5</sub>	CeHs	CeHs	CeHs
Example No.	630	631	632	633	634	635	636

The preparation of the unsaturated polyesters of this invention is according to well known techniques in the art as described, for example, in U.S. Patents: 3,642,672; 3,549,586; 4,299,927; and 4,355,136. It is preferred that these polyesters have an acid number of from about 10 to about 28, an inherent viscosity of from about 0.05 to about 0.25, and a number average molecular weight of from about 1100 to about 3800. Typical colored polyester material prepared in accordance with this invention are as follows:

#### Example 637

Preparation of Unsaturated Polyester Material from Neopentyl Glycol, Isophthalic Acid, and Maleic Anhydride Copolymerized with Methine Colorant and Cured With Styrene

The reaction apparatus comprising a one-litre flask is fitted with a stirrer, thermometer, nitrogen inlet tube, and heated Vigreux column. The top of the Vigreux column is also fitted with a Dean-Stark trap and cold water condenser. The flask is charged with 251.6 g of neopentyl glycol (2.415 mol), 191.0 g of isophthalic acid (1.15 m), 0.0951 g (200 ppm) of the reactive methine compound

and 0.55 g of dibutyltin oxide. The flask is then heated to reflux and held at this temperature until the theoretical amount of distillate is collected from this esterification stage. The reaction system is cooled to 145°C and 112.8 g of maleic anhydride (1.15 m) and 0.055 g of toluhydroquinone are added. The esterification and polycondensation reactions are continued for one hour at 175°C, then for one hour at 185°C, and then at 195°C until an acid number of 18.1 for the unsaturated polyester is obtained. The inherent viscosity of this polyester is 0.133, the number average molecular weight is 2640 and the color is bright red-orange. Sufficient of this polyester material is blended or dissolved in styrene monomer to give 40 wt.% monomer and the system then blended with 1 wt% benzoyl peroxide. One-eighth inch thick sheet castings are prepared by decanting the blende between glass plates separated by \(\frac{1}{2}\text{-inch thick gasket.}\) The blend is cured by heating for two hours at 70°C, then for one hour at 100°C, then for two hours at 125°C, and then for one hour at 150°C. After cooling, the cured polyester sheet is removed and cut into bars. The flexural strength of the bars is 18.46 × 10³ psi (127 N/mm²).

#### Example 638

Preparation of Unsaturated Polyester Material from Propylene Glycol, Isophthalic Acid, and Maleic Anhydride Copolymerized With Methine Colorant and Cured With Styrene

The following components are charged into the equipment described in Example 801:

192.5 g propylene glycol (2.53 mol); 191.0 g isophthalic acid (1.15 mol); 0.50 g dibutyltin oxide;) and

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These components are reacted as described in Example 801 until the theoretical amount of distillate is collected. The reaction is cooled to 145°C and 112.8 g maleic anhydride (1.15 mol) and 0.05 g of toluhydroquinone are added. The reaction is continued for one hour at 175°C, then for one hour at 185°C, and then at 195°C until an acid number of 14.1 for the unsaturated polyester is obtained. The inherent viscosity of this polyester is 0.11, the number average molecular weight is 1912, and the color is yellow. A curable blend of this unsaturated polyester and sheet casting and bars thereof were prepared as in Example 801. The bars had a flexural strength of 18.60 × 10³ psi (128 N/mm²).

The above inherent viscosities, acid numbers, number average molecular weights, and flexural strengths were determined as follows:

Acid number by ASTM D-1639-70;

Number Average Moplecular Weight by ASTM D—08.03 (Gel Permeation Chromatography); Flexural Strength by ASTM D—790—81;

Inherent Viscosity according to ASTM D2857—70 procedure in a Wagner Viscometer of Lab Glass Inc. of Vineland, N.J. having a 1/2 ml capilary bulb, using a polymer concentration of 0.5% by weight in 60/40 by weight, phenol/tetrachloroethane solvent. The procedure comprises heating the polymer/solvent system at

120°C for 15 minutes to enhance dissolution of the polymer, cooling the solution to 25°C and measuring the time of flow at 25°C. The I.V. is calculated from the equation

where:

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 $\eta$  = Inherent viscosity at 25°C at a polymer concentration of 0.5 g/100 ml of solvent;

In = Natural logarithm;

t<sub>s</sub> = Sample flow time;

 $\tilde{t_o}$  = Solvent-blank flow time; and

C = Concentration of polymer in grams per 100 ml of solvent = 0.50.

#### Claims

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1. A colored composition comprising unsaturated polyester material, wherein the polyester has an I.V. of 0.05 to 0.25, an acid number of 10 to 28, and a number average molecular weight of from 1100 to 3800, having copolymerized therein a total of from 1.0 to 5000 ppm of at least one methine moiety, said moiety absorbing in the range of from 320 nm to 650 nm and being nonextractable from said polyester material, wherein each methine moiety is derived from a reactive compound having the formula

45 wherein each A is selected from the following radicals:

$$(R) = \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1$$

$$(R) \xrightarrow{\stackrel{\circ}{\mathbf{n}}} \stackrel{\circ}{\mathbf{n}} \stackrel{$$

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$$(R)_{n} \stackrel{\text{if}}{\underset{R_{1}}{\overset{\text{o}}{\underset{R}{\overset{\text{o}}{\underset{R_{1}}{\overset{\text{o}}{\underset{R_{1}}{\overset{\text{o}}{\underset{R_{1}}{\overset{\text{o}}{\underset{R}{\overset{\text{o}}{\underset{R_{1}}{\overset{\text{o}}{\underset{R_{1}}{\overset{\text{o}}{\underset{R_{1}}{\overset{\text{o}}{\underset{R}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}}{\underset{R}}{\overset{\text{o}}}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}}}{\overset{\text{o}}}}{\overset{\text{o}}}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}}}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}}}}{\overset{\text{o}}}}}{\overset{\text{o}}{\overset{\text{o}}{\underset{R}}}}}{\overset{\text{o}}{\underset{R}}{\overset{\text{o}}}}}{\overset{\text{o}}{\underset{R}}{\overset{o}}{\overset{\{o}}}{\overset{\text{o}}}}}{\overset{\overset{\{o}}{\underset{R}}{\overset{\{o}}}}{\overset{\{o}}}}}{\overset{\overset{\{o}}{\underset{R}}{\overset{\{o}}}{\overset{\{o}}{\overset{\{o}}}}{\overset{\overset{\{o}}}{\underset{R}}{\overset{\{o}}}}}{\overset{\overset{\{o}}}{\underset{R}}{\overset{\overset{\{o}}}{\overset{\{o}}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}{\overset{\{o}}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}{\overset{\{o}}}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}}{\overset{\overset{\{\{o}}}}}{\overset{\overset{\{o}}}{\overset{\overset{\{o}}}}{\overset{\overset{\{o}}}}}{\overset{\overset{\{\{o}}}}}}{\overset{\overset{\{\{o}}}}{\overset{\overset{\{o}}}}}{\overset{\overset{\{\{o}}}{\overset{\overset{\{o}}$$

$$R_{10}$$
 $R_{10}$ 
 $R_{10}$ 
 $R_{10}$ 
 $R_{10}$ 
 $R_{11}$ 
 $R_{11}$ 
 $R_{11}$ 

$$R_4$$
 $R_5$ 
 $R_6$ 
 $R_1$ 
 $R_{10}$ 
 $R_{10}$ 

wherein:

R and R' are selected from hydrogen, fluorine, chlorine, bromine, alkyl, alkoxy, phenyl, phenoxy, alkyltio, and arylthio; n is 0, 1, 2;

R<sub>1</sub> and R<sub>2</sub> are selected from hydrogen; cycloalkyl; cycloalkyl substituted with one or two of alkyl, —OH, alkoxy, halogen, or hydroxy substituted alkyl; phenyl; phenyl substituted with alkyl, alkoxy, halogen, alkanoylamino, carboxy, cyano, or alkoxycarbonyl; straight or branched lower alkenyl; straight or branched alkyl of 1—8 carbons and such alkyl substituted with the following: hydroxy; halogen; cyano; succinimido; hydroxysuccinimido; acyloxysucinimido; glutarimido; phenylcarbamoyloxy; phthalimido; 4-carboxyphthalimido; phthalimidino; 2-pyrrolidono; cyclohexyl; phenyl; phenyl substituted with alkyl, alkoxy, halogen, hydroxy alkanoylamino, carboxy, cyano, or alkoxycarbonyl; alkylsulfamoyl; vinylsulfonyl; acrylamido; sulfamyl; benzoylsulfonicimido; alkylsulfonamido; phenylsulfonamido; alkoxycarbonylamino; alkylcarbamoyloxy; alkoxycarbonyloxy; alkenylcarbonylamino; groups of the formula

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wherein Y is -NH-

25 —O—, —S—, or —CH<sub>2</sub>O—; —S—R<sub>14</sub>; SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SR<sub>14</sub>; wherein R<sub>14</sub> is alkyl, phenyl phenyl substituted with halogen, alkyl, alkoxy, alkanoylamino, cyano, or alkoxycarbonyl; pyridyl; pyrimidinyl; benzoxazolyl; benzimidazolyl; benzothiazolyl; radicals of the formulae

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—OSR<sub>16</sub>; —NHXR<sub>16</sub>; —X—R<sub>16</sub>; —CONR<sub>15</sub>R<sub>15</sub>; and —SO<sub>2</sub>NR<sub>15</sub>R<sub>16</sub>; wherein R<sub>16</sub> is selected from H, aryl, alkyl, and alkyl substituted with halogen, —OH, phenoxy, aryl, —CN, cycloalkyl, alkylsulfonyl, alkylthio, alkanoyloxy, or alkoxy; X is —CO—, —COO—, or —SO<sub>2</sub>—; R<sub>16</sub> is selected from alkyl and alkyl substituted with halogen, hydroxy, phenoxy, aryl, cyano, cycloalkyl, alkylsulfonyl, alkylthio, alkanoyloxy, and alkoxy; and when X is —CO—, R<sub>16</sub> also can be hydrogen, amino, alkenyl, alkylamino, dialkylamino, arylamino, aryl, or furyl; alkoxy; alkoxy substituted with hydroxy, cyano, alkanoyloxy, or alkoxy; phenoxy; phenoxy substituted with one or more of alkyl, carboxy, alkoxy, carbalkoxy, or halogen; R<sub>1</sub> and R<sub>2</sub> can be a single combined group such as pentamethylene, tetramethylene, ethyleneoxy ethylene, ethylene

XR<sub>17</sub> | ethylene—N-ethylene

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which, with the nitrogen to which it is attached, forms a ring;  $R_{17}$  is alkyl, aryl, or cycloalkyl;  $R_3$  is alkylene, arylene, aralkylene, alkyleneoxy, or alkyleneoxyalkylene;

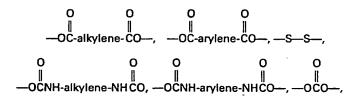
Z is a direct single bond, OCO, O, S, SO<sub>2</sub>, R<sub>17</sub>SO<sub>2</sub>N=,

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arylene, or alkylene;

R<sub>4</sub>, R<sub>5</sub>, and R<sub>6</sub> are each selected from hydrogen and alkyl;

 $R_7$  is carboxy, carbalkoxy, or  $(R)_n$ ;

R<sub>10</sub> is hydrogen, alkyl, and aryl;

R<sub>8</sub> and R<sub>9</sub> are each selected from hydrogen and substituted or unsubstituted alkyl, aryl, or cycloalkyl;

R<sub>11</sub> and R<sub>12</sub> are each selected from hydrogen, alkyl, hydroxyl, or acyloxy;

B represents the atoms necessary to complete a five or six membered ring and is selected from

each P and Q are selected from cyano, carbalkoxy, carbaryloxy, carbaralkyloxy, carbamyl, carboxy, N-alkylcarbamyl, N-arylcarbamyl, N,N-dialkylcarbamyl, N-arylcarbamyl, N-cyclohexylcarbamyl, aryl, 2-benzoxazolyl, 2-benzothiazolyl, 2-benzimidazolyl, 1,3,4-thiadiazol-2-yl, 1,3,4-oxadiazol-2-yl, SO<sub>2</sub> alkyl, SO<sub>2</sub> aryl, and acyl, or P and Q may be combined as

wherein  $R_{17}$  is defined above and  $R_{18}$  is CN, COOH, CO $_2$  alkyl, carbamyl, or N-alkylcarbamyl;

wherein at least one of A, P, and Q for each dye molecule must be or bear a condensable group selected from carboxy, carbalkoxy, carbaryloxy, N-alkylcarbamyloxy, acyloxy, chlorocarbonyl, carbamyloxy, N-(alkyl)<sub>2</sub>carbamyloxy, amino, alkylamino, hydroxyl, N-phenylcarbamyloxy, cyclohexanoyloxy, and carbocyclohexyloxy; and

wherein in the above definitions, each alkyl, aryl, or cycloalkyl moiety or portion of a group or radical may be substituted where appropriate with hydroxyl, acyloxy, alkyl, cyano, alkoxycarbonyl, halogen, alkoxy, or aryl, aryloxy, or cycloalkyl.

2. The composition of claim 1 wherein the polyester acid component is comprised of 40—60 mole% isophthalic acid and conversely 60—40 mole% of either or a mixture of maleic fumaric acid, and the alcohol component is comprised of propylene glycol, neopentyl glycol, or mixtures thereof.

3. The composition of claim 3 wherein the polyester acid component is comprised of isophthalic acid and maleic acid, and the alcohol is neopentyl glycol or neopentyl glycol mixed with less than about 75 mole% propylene glycol.

4. The composition of claim 1 wherein the reactive compound has the formula

5. The composition of claim 4 wherein: R is H, alkyl, halogen or alkoxy; and

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R<sub>1</sub> and R<sub>2</sub> are each selected from H, alkyl, cycloalkyl, cycloalkyl substituted with one or more of alkyl, OH, CN, alkoxy, carbalkoxy or alkanoyloxy, and alkyl substituted with one or more of OH, CN, alkanoyloxy, carbalkoxy, aryl, substituted aryl, alkoxy, alkoxyalkoxy, halogen, succinimido or carbamyl.

6. The composition of claim 1 wherein the reactive compound has the formula

7. The composition of claim 6 where:

R is H, alkyl, halogen or alkoxy;

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R<sub>1</sub> is selected from H, alkyl, cycloalkyl, cycloalkyl substituted with one or more of alkyl, OH, CN, alkoxy, carbalkoxy or alkanoyloxy, and alkyl substituted with one or more of OH, CN, alkanoyloxy, carbalkoxy, aryl, substituted aryl, alkoxy, alkoxy-alkoxy, halogen, succinimido or carbamyl; and

R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> are each H or alkyl.

8. The composition of claim 1 wherein the reactive compound has the formula

9. The composition of claim 8 wherein:

R and R' are each selected from H, alkyl, halogen and alkoxy; and

R<sub>1</sub> is H, alkyl, cycloalkyl, cycloalkyl substituted with one or more of alkyl, OH, CN, alkoxy, carbalkoxy or alkanoyloxy, and alkyl substituted with one or more of OH, CN, alkanoyloxy, carbalkoxy, aryl, substituted aryl, alkoxy, alkoxyalkoxy, halogen, succinimido or carbamyl.

10. The composition of claim 1 wherein the reactive compound has the formula

11. The composition of claim 10 wherein:

each R is H, alkyl, halogen or alkoxy; each R, is H, alkyl, cycloalkyl, cycloalkyl substituted with one or more of alkyl, OH, CN, alkoxy, carbalkoxy or alkanoyloxy, and alkyl substituted with one or more of OH, CN, alkanoyloxy, carbalkoxy, aryl, substituted aryl, alkoxy, alkoxyalkoxy, halogen, succinimido or carbamyl;

12. The composition of claim 1 wherein the condensable group is one or more of carboxy, carbalkoxy or hydroxy.

13. The composition of claim 1 wherein the reactive compound is

14. The composition of claim 1 wherein the reactive compound is

$$(CH_3)_2N-(CH_2)_{CO_2C_2H_5}$$

15. The composition of claim 1 wherein the reactive compound is

16. The composition of claim 1 wherein the reactive compound is

17. The composition of claim 1 wherein the reactive compound is

$$(CH_3COCH_2CH_2)_2-N-CH=CH_3$$

18. The composition of claim 1 wherein the reactive compound is

- 19. The composition of any of claims 1-3 blended with a curing agent.
- 20. The cured composition of claim 19.
- 21. Formed articles of the cured composition of claim 20.

## Patentansprüche

1. Farbige Zusammensetzung mit einem ungesättigten Polyestermaterial, in der der Polyester eine I.V. von 0,05 bis 0,25, eine Säurezahl von 10 bis 28 sowie eine mittlere Molekulargewichtszahl von 1100 bis 3800 hat, und der eincopolymerisiert insgesamt 1,0 bis 5000 ppm mindestens einer Methingruppierung enthält, die im Bereich von 320 nm bis 650 nm absorbiert und aus dem Polyestermaterial nicht extrahierbar ist, wobei jede Methingruppierung sich von einer reaktiven Verbindung mit der Formel

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15 ableitet, wobei jedes A aus einem der folgenden Reste ausgewählt ist:

$$(R) \xrightarrow{n} (R)_{n} (R)_{n}$$

$$(R) = \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \end{pmatrix} \begin{pmatrix} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1$$

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R und R' ausgewählt sind aus Wasserstoff, Fluor, Chlor, Brom, Alkyl, Alkoxy, Phenyl, Phenoxy, Alkylthio und Arylthio; und n gleich 0, 1 oder 2 ist;

R<sub>1</sub> und R<sub>2</sub> ausgewählt sind aus Wasserstoff, Cycloalkyl; Cycloalkyl, das substituiert ist durch ein oder zwei Alkyl, OH-, Alkoxy, Halogen, oder Hydro-substituiertem Alkyl; Phenyl, Phenyl, substituiert durch Alkyl, Alkoxy, Halogen, Alkanoylamino, Carboxy, Cyano oder Alkoxycarbonyl; geradkettigem oder verzweigtkettigem kurzkettigen Alkenyl; geradkettigem oder verzweigtkettigem Alkyl mit 1-8 Kohlenstoffatomen und solchem Alkyl, das substituiert ist durch: Hydroxy; Halogen; Cyano; Succinimido; Hydroxysuccinimido; Acyloxysuccinimido; Glutarimido; Phenylcarbamoyloxy; Phthalimido; 4-Carboxyphthalimido; Phthalimidino; 2-Pyrrolidono; Cyclohexyl; Phenyl; Phenyl substituiert mit Alkyl, Alkoxy, Halogen, Hydroxyalkanoylamino, Carboxy, Cyano oder Alkoxycarbonyl; Alkylsulfamoyl; Vinylsulfonyl; Acrylamido; Sulfamyl, Benzoylsulfonicimido; Alkylsulfonamido, Phenylsulfonamido; Alkoxycarbonylamino, Alkylcarbamoyloxy; Alkoxycarbonyl; Alkoxycarbonyloxy; Alkenylcarbonylamino; Gruppen der Formel

in der Y gleich —NH—, —N-alkyl, —O—, —S—, oder — $CH_2O$ — ist; — $SR_{14}$ ;  $SO_2CH_2CH_2SR_{14}$ ; worin  $R_{14}$  gleich Alkyl, Phenyl, Phenyl substituiert mit Halogen, Alkyl, Alkoxy, Alkanoylamino, Cyano oder Alkoxycarbonyl ist; Pyridyl; Pyrimidinyl; Benzoxazolyl, Benzimidazolyl; Benzothiazolyl; Resten der Formeln

-OXR<sub>16</sub>; —NHXR<sub>16</sub>; —X—R<sub>16</sub>; —CONR<sub>15</sub>R<sub>15</sub>; und —SO<sub>2</sub>NR<sub>15</sub>R<sub>15</sub>; worin R<sub>15</sub> ausgewählt ist aus H, Aryl, Alkyl, und Alkyl substituiert mit Halogen, -OH, Phenoxy, Aryl-, -CN, Cycloalkyl, Alkylsulfonyl, Alkylthio, Alkanoyloxy oder Alkoxy; X ist gleich —CO—, —COO—, oder —SO<sub>2</sub>—, R<sub>16</sub> ist, ausgewählt aus Alkyl und Alkyl, substituiert mit Halogen, Hydroxy, Phenoxy, Aryl, Cyano, Cycloalkyl, Alkylsulfonyl, Alkylthio, Alkanoyloxy, und Alkoxy, wobei gilt, daß wenn X gleich —CO— ist, R<sub>16</sub> ferner stehen kann für Wasserstoff, Amino, Alkenyl, Alkylamino, Dialkylamino, Arylamino, Aryl oder Furyl; Alkoxy, substituiert mit Hydroxy, Cyano, Alkanoyloxy oder Alkoxy; Phenoxy; Phenoxy, substituiert mit einem oder mehreren Alkyl, Carboxy, Alkoxy, Carbalkoxy oder Halogen; und worin R<sub>1</sub> und R<sub>2</sub> eine einzelne kombinierte Gruppe bilden können, z.B. Pentamethylen, Tetramethylen, Ethylenoxyethylen, Ethylensulfonylethylen oder

die mit dem Stickstoff, an den sie gebunden ist, einen Ring bildet, wobei R<sub>17</sub> für Alkyl, Aryl oder Cycloalkyl steht;

R<sub>3</sub> steht für Alkylen, Arylen, Aralkylen, Alkylenoxy oder Alkylenoxyalkylen; Z ist eine direkte einfache Bindung oder OCO, O, S, SO<sub>2</sub>, R<sub>17</sub>SO<sub>2</sub>N=,

Arylen oder Alkylen;

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 $R_{\text{4}},\,R_{\text{5}}$  und  $R_{\text{6}}$  sind jeweils ausgewählt aus Wasserstoff und Alkyl;

R7 steht für Carboxy, Carbalkoxy oder (R),

R<sub>10</sub> ist Wasserstoff, Alkyl oder Aryl;

 $R_{ extsf{g}}$  ud  $R_{ extsf{g}}$  sind ausgewählt aus Wasserstoff und substituiertem oder unsubstituiertem Alkyl, Aryl oder Cycloalkyl;

R<sub>11</sub> und R<sub>12</sub> sind jeweils ausgewählt aus Wasserstoff, Alkyl, Hydroxyl oder Acyloxy;

B steht für die Atome, die erforderlich sind, um einen fünf- oder sechsgliedrigen Ring zu vervollständigen und ist ausgewählt aus: 20

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$$\mathbb{R}^{25}$$
 $\mathbb{R}^{7}$ 
 $\mathbb{R}^{7}$ 

P und Q sind jeweils ausgewählt aus Cyano, Carbalkoxy, Carbaryloxy, Carbaralkyloxy, Carbamyl, Carboxy, N-Alkylcarbamyl, N-Alkyl-N-arylcarbamyl, N-N-Dialkylcarbamyl, N-Arylcarbamyl, N-N-Dialkylcarbamyl, N-Arylcarbamyl, N-N-Dialkylcarbamyl, N-Dialkylcarbamyl, N-N-Dialkylcarbamyl, N-N Cyclohexylcarbamyl, Aryl, 2-Benzoxazolyl, 2-Benzothiazoyl, 2-Benzimidazolyl, 1,3,4-Thiadiazol-2-yl, 1,3,4-Oxadiazol-2-yl, SO<sub>2</sub>-Alkyl, SO<sub>2</sub>-Aryl und Acyl oder P und Q können kombiniert sein zu

worin R<sub>17</sub> die bereits angegebene Bedeutung hat und R<sub>18</sub> steht für-CN, —COOH, —CO<sub>2</sub>-alkyl, Carbamyl oder N-alkylcarbamyl;

wobei mindestens einer der Reste A, P und Q für jedes Farbstoffmolekül eine kondensierbare Gruppe,

ausgewählt aus den folgenden Gruppen sein muß oder eine solche Gruppe tragen muß: Carboxy, Chlorocarbonyl, Carbamyloxy, N-Carbaryloxy, N-Alkylcarbamyloxy, Acyloxy, (Alkyl)<sub>2</sub>carbamyloxy, Amino, Alkylamino, Hydroxyl, N-Phenylcarbamyloxy, Cyclohexanoyloxy und Carbocyclohexyloxy;

und worin in den angegebenen Definitionen jeder Alkyl-, Aryl- oder Cycloalkylrest gegebenenfalls substituiert sein kann mit Hydroxyl, Acyloxy, Alkyl, Cyano, Alkoxycarbonyl, Halogen, Alkoxy oder Aryl, Aryloxy oder Cycloalkyl.

2. Zusammensetzung nach Anspruch 1, in der die Polyester-Säurekomponente zu 40-60 Mol-% aus lsophthalsäure und zu 60-40 Mol-% aus entweder Maleinsäure oder Fumarsäure oder einer Mischung hiervon besteht und die Alkoholkomponente aus Propylenglykol, Neopentylglykol oder einer Mischung

3. Zusammensetzung nach Anspruch 2, in der die Polyester-Säurekomponente aus Isophthalsäure und Maleinsäure und die Alkoholkomponente aus Neopentylglykol, oder Neopentylglykol, vermischt mit weniger als etwa 75 Mol-% Proylenglykol besteht.

4. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung die folgende Formel hat;

5. Zusammensetzung nach Anspruch 4, in der bedeuten:

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R gleich Wasserstoff, Alkyl, Halogen oder Alkoxy und R<sub>1</sub> und R<sub>2</sub> jeweils ausgewählt sind aus Wasserstoff, Alkyl, Cycloalkyl, Cycloalkyl substituiert mit einem oder mehreren Alkyl, —OH, —CN, Alkoxy, Carbalkoxy, oder Alkanoyloxy und Alkyl substituiert mit einem

oder mehreren —OH, —CN, Alkanoyloxy, Carbalkoxy, Aryl, substituiertem Aryl, Alkoxy, Alkoxyalkoxy, Halogen, Succinimido oder Carbamyl.

6. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung der folgenden Formel entspricht:

7. Zusammensetzung nach Anspruch 6, worin bedeuten:

R Wasserstoff, Alkyl, Halogen oder Alkoxy;

R<sub>2</sub> Wasserstoff, Alkyl, Cycloalkyl, Cycloalyl substituiert mit einem oder mehreren Alkyl, —OH, —CN, Alkoxy, Carbalkoxy oder Alkanoyloxy und Alkyl substituiert mit einem oder mehreren -OH, -CH, Alkanoyloxy, Carbalkoxy, Aryl, substituiertem Aryl, Alkoxy, Alkoxy-alkoxy, Halogen, Succinimido oder Carbamyl und

 $R_4$ ,  $R_5$  und  $R_6$  jeweils Wasserstoff oder Alkyl.

8. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung der folgenden Formel entspricht:

9. Zusammensetzung nach Anspruch 8, in der bedeuten:

R und R' jeweils Wasserstoff, Alkyl, Halogen oder Alkoxy und

R<sub>1</sub> Wasserstoff, Alkyl, Cycloalkyl, Cycloalkyl substituiert mit einem oder mehreren Alkyl-, —OH, —CN, Alkoxy, Carbalkoxy oder Alkanoyloxy und Alkyl substituiert mit einem oder mehreren —OH, —CN, Alkanoyloxy, Carbalkoxy, Aryl, substituiertem Aryl, Alkoxy, Alkoxyalkoxy, Halogen, Succinimido oder Carbamyl.

10. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung der folgenden Formel entspricht:

11. Zusammensetzung nach Anspruch 10, worin bedeuten:

R jeweils Wasserstoff, Alkyl, Halogen oder Alkoxy;

R<sub>1</sub> jeweils Wasserstoff, Alkyl, Cycloalkyl, Cycloalkyl substituiert mit einem oder mehreren Alkyl, —OH, -CN, Alkoxy, Carbalkoxy oder Alkanoyloxy und Alkyl substituiert mit einem oder mehreren —OH, —CN, Alkanoyloxy, Carbalkoxy, Aryl, substituiertem Aryl, Alkoxy, Alkoxyalkoxy, Halogen, Succinimido oder Carbamyl; und

12. Zusammensetzung nach Anspruch 1, in der die kondensierbare Gruppe aus einer oder mehreren Carboxy-, Carbalkoxy- oder Hydroxygruppen besteht.

13. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung besteht aus:

14. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung besteht aus:

$$(CH_3)_2N-CH=CC_2C_2H_5$$

15. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung besteht aus:

16. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung besteht aus:

17. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung besteht aus:

$$(CH_3COCH_2CH_2)_2-N-CH= CH_3 CH_3$$

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18. Zusammensetzung nach Anspruch 1, in der die reaktive Verbindung besteht aus:

- 19. Zusammensetzung nach einem der Ansprüche 1-3, vermischt mit einem Härungsmittel.
- 20. Die gehärtete Zusammensetzung nach Anspruch 19.
- 21. Formkörper, hergestellt aus der gehärteten Zusammensetzung nach Anspruch 20.

#### Revendications

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1. Composition colorée comprenant un polyester insaturé, ayant une viscosité inhérente comprise entre 0,05 et 0,25, un indice d'acidité compris entre 10 et 28 et un poids moléculaire moyen en nombre compris entre 1100 et 3800, dans lequel est copolymérisé un total de 1,0 à 5000 ppm d'au mons un groupement méthine, ledit groupement méthine absorbant dans la région du spectre comprise entre 320 nm et 650 nm et étant non extractible dudit polymère, et dans lequel chaque groupement méthine est dérivé d'un composé réactif ayant la formule:

PC=CH-A, A-CH=
$$\overset{p}{C}$$
- $\overset{p}{C}$ -CH-A, (R)<sub>n</sub>

$$\overset{p}{Q}$$
C=HC- $\overset{p}{Q}$ - $\overset{$ 

où chaque A est choisi parmi les radicaux suivants:

(R) 
$$\frac{1}{n}$$
 (R)  $\frac{1}{n}$  (

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où:

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R et R' sont choisis parmi les atomes d'hydrogène, de fluor, de chlore, de brome, les radicaux alkyle, alkoxy, phényle, phénoxy, alkylthio, et arylthio; n est 0, 1, 2;

R₁ et R₂ sont choisis parmi un atome d'hydrogène; un radical cycloalkyle; cycloalkyle substitué par un ou deux alkyle, -OH, alkoxy, halogène ou alkyle substitué par un groupe hydroxy; un radical phényle; phényle substitué par un alkyle, alkoxy, halogène, alkanoylamino, carboxy, cyano, ou alkoxycarbonyle; un radical alkènyle inférieur droit ou ramifié; un radical alkyle droit ou ramifié de 1 à atomes de carbone et un radical alkyle substitué par les groupes suivants; hydroxy; halogène; cyano; succinimido; hydroxysuccinimido; acyloxysuccinimido; glutarimido; phénylcarbamoyloxy; phtalimido; 4carboxyphtalimido; phtalimidono; 2-pyrrolidono; cyclohexyle; phényle; phényle substitué par un groupe alkyle, alkoxy, halogène hydroxy alkanoylamino, carboxy, cyano, ou alkoxycarbonyle; alkylsulfamoyle;

vinylsulfonyle; acrylamido; sulfamyle; benzoylsulfonicimido; alkylsulfonamido; phénylsulfonamido; alkoxycarbonylamino; alkylcarbamoyloxy; alkoxycarbonyle; alkoxycarbonyloxy; alkénylcarbonylamino; les groupes de formule:

où Y est —NH—, —N-alkyle, —O—, —S—, ou — $CH_2O$ —; —S— $R_{14}$ ;  $SO_2CH_2CH_2SR_{14}$ ; où  $R_{14}$  est un radical alkyle, phényle, phényle substitué par un halogène, alkyle, alkoxy, alkanoylamino, cyano, ou alkoxycarbonyle; pyridyle; pyrimidinyle; benzoxazolyle; benzimidazolyle; benzothiazolyle; ou un radical de formule:

 $-OXR_{16}$ ;  $-NHXR_{16}$ ;  $-X-R_{16}$ ;  $-CONR_{15}R_{15}$ ; et  $-SO_2NR_{15}R_{15}$ ; où  $R_{15}$  est choisi parmi un atome d'hydrogène, un groupe aryle, alkyle, et alkyle substitué par un halogène, -OH, phénoxy, aryle, -CN, cycloalkyle, alkylsulfonyle, alkylthio, alkanoyloxy, ou alkoxy; X est -CO-, -COO-, ou  $-SO_2-$ ;  $R_{16}$  est choisi parmi les radicaux alkyle et alkyle substitué par un halogène, hydroxy, phénoxy, aryle, cyano, cycloalkyle, alkylsulfonyle, alkylthio, alkanoyloxy, et alkoxy; et lorsque X est —CO—, R<sub>16</sub> peut aussi être un atome d'hydrogène, un radical amino, alkényle, alkylamino, dialkylamino, arylamino, aryle ou furyle; alkoxy; alkoxy substitué par un hydroxy, cyano, alkanoyloxy, ou alkoxy; phénoxy; phénoxy substitué par un ou plusieurs alkyle, carboxy, alkoxy, carbalkoxy, ou halogène; R1 et R2 peuvent former un groupe unique tel que pentaméthylène, tétraméthylène, éthylèneoxyéthylène, éthylène sulfonyléthylène, ou

qui, avec l'atome d'azote auquel il est attaché forme un cycle; R<sub>17</sub> est alkyle, aryle ou cycloalkyle;

R<sub>3</sub> est alkylène, arylène, aralkylène, alkylèneoxy, ou alkylèneoxyalkylène;

Z est une liaison simple, OCO, O, S, SO<sub>2</sub>, R<sub>17</sub>SO<sub>2</sub>N=,

arylène, ou alkylène;

R<sub>4</sub>, R<sub>5</sub>, et R<sub>6</sub> sont chacun choisis parmi un atome d'hydrogène et un radical alkyle;

R<sub>7</sub> est un radical carboxy, carbalkoxy, ou (R)<sub>n</sub>;

R<sub>10</sub> est un atome d'hydrogène, un radical alkyle, et aryle;

 $R_{\theta}$  et  $R_{\theta}$  chacun choisis parmi un atome d'hydrogène, un radical alkyle, aryle ou cycloalkyle substitué

R<sub>11</sub> et R<sub>12</sub> sont chacun choisis parmi un atome d'hydrogène, un radical alkyle, hydroxyle ou acycloxy B représente le nombre d'atomes nécessaire pour compléter un cycle à 5 ou 6 chaînons et est choisi parmi;

$$R_7$$
  $R_7$   $R_7$   $R_7$ 

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chacun des P et Q est choisi parmi les radicaux cyano, carbalkoxy, carbaryloxy, carbaralkyloxy, carbamyle, carboxy, N-alkylcarbamyle, N-alkyl-N-arylcarbamyle, N,N-dialkylcarbamyle, N-arylcarbamyle, Ncyclohexylcarbamyle, aryle, 2-benzoxazolyle, 2-benzothiazolyle 2-benzimidazolyle, 1,3,4-thiadiazol-2-yle, 1,3,4-oxadiazol-2-yle, SO<sub>2</sub>-alkyle, SO<sub>2</sub>-aryle, et acyle, ou P et Q peuvent être combinés sous la formule

où R<sub>17</sub> est défini comme ci-dessus et R<sub>18</sub> est CN, COOH, CO<sub>2</sub>-alkyle, carbamyle, ou N-alkylcarbamyle;

où au moins un des À, P, et Q pour chaque molécule de colorant peut être ou peut porter un groupe condensable choisi parmi les groupes carboxy, carbalkoxy, carbaryloxy, N-alkylcarbamyloxy, acyloxy, N-(alkyl)<sub>2</sub>-carbamyloxy, amino, alkylamino, chlorocarbonyle, carbamyloxy, phénylcarbamyloxy, cyclohexanoyloxy, et carbocyclohexyloxy; et

où dans les définitions ci-dessus, chaque groupement ou portion de groupement ou radical alkyle, aryle, ou cycloalkyle peut être substitué là où c'est possible par un radical hydroxyle, acyloxy, alkyle, cyano, alkoxycarbonyle, un atome d'halogène, un radical alkoxy, ou aryle, aryloxy, ou cycloalkyle.

2. Composition selon la revendication 1, dans lequel la composante acide du polyester comprend de 40 à 60% en poids d'acide isophtalique, et inversement 60 à 40% soit d'acide maléique soit d'acide fumarique, soit d'un mélange d'acide maléique et d'acide fumarique, et la composante alcool du polyester comprend du polypropylène glycol, du néopentyl glycol ou des mélanges de ces derniers.

3. Composition selon la revendication 2, dans lequel la composante acide du polyester comprend de l'acide isophtalique et de l'acide maléique et l'alcool est le néopentyl glycol, où du néopentyl glycol

mélange à au moins d'environ 75% en moles de propylène glycol. 4. Composition selon la revendication 1, dans laquelle le composé réactif a la formule:

5. Composition selon la revendication 4, dans laquelle;

R est H, alkyle, halogène ou alkoxy; et

 $R_1$  et  $R_2$  sont chacun séparément choisis parmi H alkyle, cycloalkyle, cycloalkyle substitué par un ou plusieurs groupes alkyle, OH, CN, alkoxy, carbalkoxy ou alkanoyloxy, et alkyle substitué par un ou plusieurs OH, CN, alkanoyloxy, carbalkoxy, aryle, aryle substitué, alkoxy, alkoxyalkoxy, halogène, succinimido ou carbamyle.

6. Composition selon la revendication 1, dans laquelle le composé réactif a la formule:

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7. Composition selon la revendication 6, dans laquelle;

R est H, alkyle, halogène ou alkoxy;

R, est choisi parmi H, alkyle, cycloalkyle, cycloalkyle substitué par un ou plusieurs alkyle, OH, CN, alkoxy, carbalkoxy ou alkanoyloxy, et alkyle substitué par un ou plusieurs OH, CN, alkanoyloxy, carbalkoxy, aryle, aryle substitué, alkoxy, alkoxyalkoxy, halogène, succinimido ou carbamyle; et

R<sub>4</sub>, R<sub>5</sub> et R<sub>6</sub> sont chacun H ou alkyle.

8. Composition selon la revendication 1, dans laquelle le groupe réactif a la formule:

9. Composition selon la revendication 10, dans laquelle R et R' sont chacun choisis parmi H, alkyle,

halogène et alkoxy; et

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 $R_1$  est H, alkyle, cycloalkyle, cycloalkyle substitué par un ou plusieurs alkyle, OH, CN, alkoxy, carbalkoxy ou alkanoyloxy, et alkyle substitué par un ou plusieurs OH, CN, alkanoyloxy, carbalkoxy, aryle, aryle substitue, alkoxy, alkoxyalkoxy, halogène, succinimido ou carbamyle.

10. Composition selon la revendication 1, dans laquelle le composé réactif a la formule:

11. Composition selon la revendication 10, dans laquelle chaque R est H, alkyle, halogène ou alkoxy; chaque R<sub>1</sub> est H, alkyle, cycloalkyle, cycloalkyle substitué par un ou plusieurs alkyle, OH, CN, alkoxy, carbalkoxy ou alkanoyloxy, et alkyle substitué par un ou plusieurs OH, CN, alkanoyloxy, carbalkoxy, aryle, aryle substitué, alkoxy, alkoxyalkoxy, halogène, succinimido ou carbamyle, et

12. Composition selon la revendication 1, dans laquelle le groupe condensable est composé d'un ou plusieurs carboxy, carbalkoxy ou hydroxy.

13. Composition selon la revendication 1, dans laquelle le composé réactif est

14. Composition selon la revendication 1, dans laquelle le composé réactif est

15. Composition selon la revendication 1, dans laquelle le composé réactif est

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16. Composition selon la revendication 1, dans laquelle le composé réactif est

17. Composition selon la revendication 1, dans laquelle le composé réactif est

$$(CH_{3}COCH_{2}CH_{2})_{2}-N-(CH_{2}CH_{3}CH_{3}CH_{2}CH_{2})_{2}-N-(CH_{3}C$$

18. Composition selon la revendication 1, dans laquelle le composé réactif est

19. Composition selon l'uen quelconque des revendications 1 à 3 en mélange avec un agent de réticulation.

20. Composition réticulée selon la revendication 19.

21. Articles formés à partir de la composition réticulée de la revendication 20.